

PB86-192267

Coal Gasification Environmental Data
Summary: Low- and Medium-Btu Wastewaters

Radian Corp., Austin, TX

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Apr 86



U.S. Department of Commerce
National Technical Information Service

NTIS

EPA/600/7-86/015a
April 1986

COAL GASIFICATION ENVIRONMENTAL DATA SUMMARY:

LOW- AND MEDIUM-BTU
WASTEWATERS

by

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EPA Contract No. 68-02-3137

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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)		
1. REPORT NO. EPA/600/7-86/015a	2.	3. RECIPIENT'S ACCESSION NO. PB86 192267/AS
4. TITLE AND SUBTITLE Coal Gasification Environmental Data Summary: Low- and Medium-Btu Wastewaters	5. REPORT DATE April 1986	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Frank J. Castaldi and F. Douglas Skinner	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation P.O. Box 9948 Austin, Texas 78766	10. PROGRAM ELEMENT NO.	
	11. CONTRACT/GRANT NO. 68-02-3137	
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Final; 9/84 - 12/85	
	14. SPONSORING AGENCY CODE EPA/600/13	
15. SUPPLEMENTARY NOTES AEERL project officer is William J. Rhodes, Mail Drop 62B, 919/541-2853.		
16. ABSTRACT The report is a compilation of environmental characterization data for wastewaters from low- and medium-Btu coal gasification facilities. Fixed-bed, entrained-bed, and ash-agglomerating fluidized-bed coal gasification processes were examined. The fixed-bed gasifiers are the Chapman, Wellman-Galusha, Riley, Foster Wheeler/STOIC, and Lurgi-type processes. The entrained-bed gasifiers are the Koppers-Totzek and Texaco processes. The KRW-PDU was used as an example of an ash-agglomerating fluidized-bed process. The types of wastewaters examined from the various coal gasification processes are product gas quench condensates, cyclone dust quench waters, ash pan waters, gas compression and cooling condensates, acid gas removal waters, and leachates from slag and ash disposal facilities. The available wastewater quality and quantity data for these aqueous waste streams are assembled, and the associated environmental significance is addressed. The report describes gasification process characteristics and how they relate to wastewater quality and discusses the biodegradability of quench condensates from the different gasifier types.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Coal Gasification Coal Waste Water Analyzing Properties	Pollution Control Stationary Sources Characterization	13B 13H 21D 14B 14G
19. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 122
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This report is a compilation of environmental characterization data for wastewaters from low- and medium-Btu coal gasification facilities. Fixed-bed, entrained-bed, and ash-agglomerating fluidized-bed coal gasification processes were examined. The fixed-bed gasifiers are the Chapman, Wellman-Galusha, Riley, Foster Wheeler/STOIC, and Lurgi-type processes. The entrained-bed gasifiers are the Koppers-Totzek and Texaco processes. The KRW-PDU was used as an example of an ash-agglomerating fluidized-bed process. The types of wastewaters examined from the various coal gasification processes are product gas quench condensates, cyclone dust quench waters, ash pan waters, gas compression and cooling condensates, acid gas removal waters, and leachates from slag and ash disposal facilities. The available wastewater quality and quantity data for these aqueous waste streams are assembled and the associated environmental significance is addressed. The report describes gasification process characteristics and how they relate to wastewater quality and discusses the biodegradability of quench condensates from the different gasifier types.

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SECTION 1

INTRODUCTION

BACKGROUND

As a result of the Energy Security Act, EPA is one of the Consulting Agencies that reviews Environmental Monitoring Outlines and Plans as required by the SFC for coal gasification projects receiving financial assistance. As part of this consultation, EPA advises on the adequacy of proposed Environmental Monitoring Plans and participates in Monitoring Review Committees for the projects.

In the past decade, EPA has conducted numerous environmental data acquisition studies at coal gasification facilities in the United States, Europe, and Africa. Both tar producing and non-tar producing coal gasification facilities were examined. Comprehensive data on the characteristics of process and waste streams have been obtained from these sampling programs. These data were used to estimate the wastewater pollutant characteristics from commercial coal gasification facilities and provide a basis for the evaluation of applicable control technologies.

The EPA's Environmental Assessment data, when properly compiled and summarized, can provide information to:

- Identify environmental and health issues requiring further definition through data acquisition at SFC-supported facilities,
- Recognize process-specific characteristics for both synfuels production and pollution control technologies which would influence the scope and areas of emphasis in the planned monitoring, and

- Define data interpretation and presentation approaches which will facilitate the evaluation of the data addressing particular areas of concern in mitigating environmental and health problems with future facilities.

In order to support this effort, several documents which address specific environmental pollutant or discharge categories characteristic of coal gasification technologies have been prepared. Areas are:

- Sulfur and nitrogen species,
- Organics,
- Trace elements,
- Solid wastes, and
- Wastewater.

The documents will present summaries of environmental data for the Chapman, Wellman-Galusha, Riley, Foster-Wheeler/STOIC, Lurgi, Lurgi-type, Koppers-Totzek, KRW Energy Systems, and Texaco gasification processes. These data are compared and contrasted in order to develop trends and/or correlations that can be used to assess the environmental impacts associated with the different coal gasification processes.

This report is a compilation of data on wastewater quality from the subject coal gasification processes. It presents background on the gasification technologies, defines major aqueous waste streams, summarizes wastewater quality and quantity data obtained from source test and evaluation studies, describes gasification process characteristics and how they relate to wastewater quality, discusses the biodegradability of quench condensate streams from the different gasifier types, and assesses environmental impacts associated with the discharge of gasifier effluents.

OBJECTIVES

The objective of this report is to present an environmental analysis of pollutant species in coal gasification wastewaters. The data available from EPA sponsored environmental assessment efforts, supplemented by literature data, are compiled, summarized, evaluated, and documented to provide:

- A consolidated summary of the available wastewater quality data for commercial-scale coal gasification processes;
- An interpretive evaluation of the data including:
 - (1) Trends in pollutant behavior between processes,
 - (2) Identification of unique or specific characteristics of individual processes,
 - (3) Identification of particular environmental issues, both those common to all processes and those unique to individual processes, and
 - (4) Recommendations for monitoring of commercial scale systems to further define environmental issues or apparent trends in pollutant behavior;
- A basis for the evaluation of synfuels facility Environmental Monitoring Plans relative to wastewater characteristics; and
- A resource for EPA Regional Offices and state agencies involved in permitting of gasification facilities.

The majority of the wastewater characterization data summarized in this report are obtained from EPA sponsored source test and evaluation studies at commercial-scale tar producing and non-tar producing coal gasification facilities. These data are supplemented with wastewater characterization and treatability information obtained from pilot-scale coal gasification technologies (e.g., KRW Energy Systems and Pittsburgh Energy Technology Center, Synthane processes).

REPORT FORMAT

The report is organized as follows:

Section 2: Conclusions,

Section 3: Summary Process Descriptions,

Section 4: Wastewater Characterization Data Summary,

Section 5: Impact of Gasification Process on Quench
Condensate Quality,

Section 6: Biooxidation of Coal Conversion Wastewaters,
and

Section 7: Impact of Coal Gasification Discharges.

SECTION 2

CONCLUSIONS

There are considerable differences in the quality of wastewaters produced from the various coal gasification processes, both between and within gasifier types. These differences are due to process configuration, gasifier operation, nature of product gas cleanup and ash removal/handling, and the feed coal used. However, representative wastewater chemistries can be established for similar gasifiers with similar product gas cleanup and ash removal/handling operations fed with similar coals. This permits a categorization of wastewaters into two functional groups: aqueous wastes from tar producing (e.g., fixed-bed) gasification and aqueous wastes from non-tar producing (e.g., ash-agglomerating, fluidized-bed and entrained-bed) gasification. That is, coal gasification processes that produce substantial quantities of phenolics, oils, and tars, and processes that produce little or none of these pollutants.

The types of wastewaters that are generated by coal gasification processes are product gas quench condensates, cyclone dust quench waters, ash pan waters, gas compression and cooling condensates, acid gas removal waters, and leachates from slag and ash disposal facilities. The severity of the contamination associated with the individual effluents will vary with the coal gasification process. However, a general assessment of pollutant strength and stream volume places the quench condensates above other aqueous waste streams as the principal wastewater source.

Quench condensates can be classified by gasifier type (in this case, fixed-bed or entrained-bed) and will have relatively consistent chemistries

for a given gasifier category. These waters are usually the largest volume aqueous waste stream from a gasification process, and in the case of fixed-bed gasifiers, they contribute substantial organic pollutant loads to wastewater treating facilities. However, these aqueous wastes can be treated for removal of most conventional pollutants by biooxidation after the appropriate pretreatment steps.

Pollutants in aqueous wastes from coal gasification processes representing the highest potential for environmental (ecological) hazard are ammonia, cyanide, phenolics, and sulfur compounds (primarily sulfide). Ammonia represents the most severe potential environmental hazard because of the toxicity of undissociated ammonia to aquatic organisms. Acute toxicity of simple cyanides to fish occurs at the low parts per billion level. Cyanide will also complex with many metals and as such, has the potential of bioaccumulating in aquatic plants and animals. Phenolic compounds can affect freshwater fishes adversely by direct toxicity to fish and fish-food organisms; by lowering the amount of available oxygen because of the high oxygen demand of the compounds and by tainting of fish flesh. The degree of hazard exhibited by sulfide to aquatic animal life is dependent on the temperature, pH, and dissolved oxygen level of the receiving water.

Most coal gasification wastewaters from both fixed-bed and entrained-bed processes can be controlled with respect to the discharge of conventional pollutants (e.g., BOD, COD, and pH). The control of selected organics and trace elements will vary with the gasification process. Fixed-bed gasifiers will need to have specific attention paid to the discharge of phenolics, polynuclear aromatic hydrocarbons, ammonia, cyanide, and numerous heavy metals. Entrained-bed gasifiers will need to have attention paid to such nonconventional pollutants as ammonia, thiocyanates, free and complexed cyanides, and boron.

SECTION 3

PROCESS DESCRIPTIONS

INTRODUCTION

This section presents brief descriptions and comparisons of the coal gasification facilities for which data are presented in this report. The following types of gasifiers and facilities are included:

- Chapman low-Btu gasifiers at Kingsport, Tennessee;
- Wellman-Galusha low-Btu gasifiers at the Bureau of Mines Twin Cities Metallurgy Research Center, Fort Snelling, Minnesota, and Glen Gery Brick Company, York, Pennsylvania;
- Riley Gas Producer low-Btu gasifier at Worcester, Massachusetts;
- Foster-Wheeler/STOIC low-Btu gasifier at the University of Minnesota, Duluth;
- Lurgi-type medium-Btu gasifiers at Kosovo, Yugoslavia;
- Kellogg-Rust/Westinghouse (KRW) medium-Btu gasifier PDU at Madison, Pennsylvania;
- Koppers-Totzek medium-Btu gasifier at Ptolemais, Greece;
- Koppers-Totzek medium-Btu gasifier at Modderfontein, South Africa; and
- Texaco medium-Btu gasifier at the Ruhrkohle/Ruhrchemie facility in Oberhausen-Holtien, Federal Republic of Germany.

Table 1 presents a summary of the features of the coal handling/preparation, coal feeding, gasification, and downstream processes (including gas cleanup and ash removal/handling) present at each facility. The similarities and differences will be discussed in more detail later; however, some of the salient differences between processes are summarized below:

- Oxygen versus Air Injection: Gasifiers that use air as their source of oxygen produce a gas having a lower calorific value than those that use pure or nearly pure oxygen. This is due to the nitrogen diluent present in air. Chapman, Wellman-Galusha, Riley and Foster-Wheeler/STOIC gasifiers are of the so-called "low-Btu" type, while Lurgi, Koppers-Totzek, and Texaco gasifiers all produce "medium-Btu" gas. The KRW gasifier PDU can be operated in either mode; the data presented here were obtained during a series of medium-Btu runs.
- Bed Type: There are three principal gasifier bed types: fixed-bed, fluidized-bed, and entrained-bed. Fixed-bed (or more properly, moving bed) gasifiers feature a layer of coal which is generally supported on a grate through which air (or oxygen) and steam are passed. The direction of movement of the coal relative to the gas is counter-current. In fluidized-bed gasifiers, the upward velocity of the gas stream is such that the fluid drag forces nearly balance the downward forces due to the weight of the coal/char particles. The particles act as if they were a turbulent fluid. In entrained-bed gasifiers, the coal and gases move in the same direction (co-current). Of the gasifiers represented here, only the KRW is a fluidized-bed gasifier; entrained-bed gasifiers include the Koppers-Totzek and Texaco gasifiers. All the rest are of the fixed-bed type.
- Single-stage versus Two-stage: In single-stage gasifiers, the raw product gas is taken off at a single location. In two-stage gasifiers, two separate raw product gas streams are generated. In a fixed-bed, two-stage design the upper gas product is richer in heavier hydrocarbon gases and aerosols formed by the release of coal volatile matter and water vapor resulting from the release of moisture in the feed coal. The lower gas product is richer in lighter combustible gases such as carbon monoxide and hydrogen. The only two-stage gasifier presented here is the Foster-Wheeler/STOIC gasifier.

TABLE 1. COMPARISON OF COAL GASIFICATION FACILITIES

	Chapman	Wellman- Galusha (Fort Snelling)	Wellman- Galusha (Glen-Gery)	Riley	Foster- Wheeler/ STOIC
<u>COAL HANDLING</u>					
Receive presized coal	X	X	X	X	X
Crush/pulverize		X			X
Screen					
Thermal drying					
Slurrying					
Air classifying					
<u>COAL FEEDING</u>					
Lock hoppers		X	X	X	X
Screw feed/entrainment					
Slurry pumping					
Barrel valve	X				
<u>GASIFICATION</u>					
Atmospheric (A)/Pressurized (P)	A	A	A	A	A
Moving- (M)/Fluid- (F)/Entrained- bed (E)	M	M	M	M	M
Thin bed (T)/Deep bed (D)	T	D	D	T	D
Slagging (S)/Agglomerating (A)/ Dry ash (D)	D	D	D	D	D
Single-stage (S)/Two-stage (T)	S	S	S	S	T
Cocurrent (C)/Counter-current (CC)	CC	CC	CC	CC	CC
Air blown (A)/O ₂ blown (O)	A	A	A	A	A
<u>GAS CLEANUP</u>					
Cyclones	X	X	X	X	X
ESP					X
Quench/Scrubbing	X				
Acid gas removal					
<u>ASH REMOVAL/HANDLING</u>					
Lockhoppers				X	X
Ash plow	X				
Slide valve		X	X		
Water quench	X	X	X	X	X
Conveyor/Drag chain	X				X

(continued)

TABLE 1. COMPARISON OF COAL GASIFICATION FACILITIES (Continued)

	Lurgi-type (Kosovo)	KRW FDU	Koppers-Totzek (Modderfontein)	Koppers-Totzek (Ptolemais)	Texaco (Ruhrchemie)
<u>COAL HANDLING</u>					
Receive presized coal	X	X	X	X	X
Crush/pulverize	X				
Screen	X				
Thermal drying	X	X	X	X	
Slurrying					X
Air classifying		X			
<u>COAL FEEDING</u>					
Lock hoppers	X	X			
Screw feed/entrainment			X	X	
Slurry pumping					X
Barrel valve					
<u>GASIFICATION</u>					
Atmospheric (A)/Pressurized (P)	P	P	A	A	P
Moving- (M)/Fluid- (F)/Entrained- bed (E)	M	F	E	E	E
Thin bed (T)/Deep bed (D)	D	D	- ^a	- ^a	- ^a
Slagging (S)/Agglomerating (A)/ Dry ash (D)	D	A	S	S	S
Single-stage (S)/Two-stage (T)	S	S	S	S	S
Cocurrent (C)/Countercurrent (CC)	CC	CC	C	C	C
Air blown (A)/O ₂ blown (O)	O	O	O	O	O
<u>GAS CLEANUP</u>					
Cyclones		X			
ESP					
Quench/Scrubbing	X	X	X	X	X
Acid gas removal	X		X	X	X
<u>ASH REMOVAL/HANDLING</u>					
Lockhoppers	X	X			X
Ash plow					
Slide valve					
Water quench	X		X	X	X
Conveyor/Drag chain	X		X	X	X

^aNot applicable.

- Atmosphere Pressure versus Elevated Pressure: Operation at elevated pressure allows the use of smaller vessels for equivalent gas production. Increased partial pressures of reactive gases may increase reaction rates and/or alter reaction equilibria, in both the gasifier and in downstream units. Additional effects of pressurized operation include:
 - reduced needs for compression of raw gas prior to downstream treatment units (e.g., physical absorption types of acid gas removal processes) or prior to injection into a pipeline transmission system.
 - generation of flash gases from depressurization of by-product liquids, resulting in an additional waste gas stream.

Of the gasifiers considered here, only three were operated at elevated pressure: the Kosovo (Lurgi-type), KRW, and Ruhrkohle/Ruhrchemie (Texaco) gasifiers. The rest were operated at or near atmospheric pressure.

The remainder of this process description section consists of two subsections: the first section discusses and compares the gasification processes (including coal preparation and coal feeding), while the second section deals with downstream processing operations.

SUMMARY AND COMPARISON OF GASIFICATION OPERATIONS

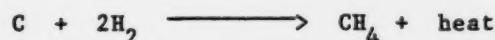
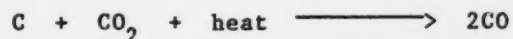
Coal gasification involves the conversion of coal to gaseous species which can be burned as fuels or which can be used as feedstocks in the formation of fuels or other products. There are several general types of phenomena which occur during coal gasification which are common to all processes. These include coal drying and devolatilization, gasification, oxidation (or combustion), water-gas shift, volatilization and reaction of coal sulfur and nitrogen, and production of unreacted residuals (ash). Each of these may occur in different areas of the gasification reactor depending on the method used to contact the coal and the reactant gases.

Drying and Devolatilization

As the coal is heated, moisture is given off and the volatile fraction undergoes pyrolysis (i.e., thermal decomposition). The composition of the volatiles (some of which may be liquids or even solids at ambient conditions) depends on a number of factors including coal rank, coal particle thermal history (e.g., heating rate, duration of heating, and final temperature reached), and composition and pressure of the ambient gas. Anthracite, for example, gives off relatively little volatile matter compared with bituminous coal or lignite. If devolatilization occurs at relatively low temperatures, the volatile fraction of a bituminous coal contains appreciable amounts of tar and oil aerosols. If devolatilization occurs at higher temperatures, these tars and oils are largely converted, by further pyrolysis and oxidation, into lighter hydrocarbons, methane, hydrogen, carbon monoxide and carbon dioxide.

Gasification

In the gasification zone, various reactions occur between carbon in the coal and hot gases present in the oxidation zone. The principle gasification reactions of interest are:

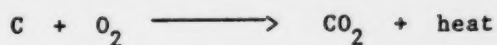


As can be seen, the energy yielding products of gasification are carbon monoxide, hydrogen, and methane. The energy required by the first two reactions is furnished by the sensible heat of the gases leaving the oxidation zone. The extent to which these competing reactions proceed to completion

depends on factors such as pressure, temperature, residence time, and reactant concentration.

Oxidation (Combustion)

Oxidation involves the heterogeneous reaction between coal, carbon, and oxygen to produce CO and CO₂:

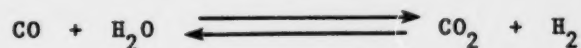


These reactions result in the release of energy that allows the gasification reactions to proceed. The ratio of carbon monoxide to carbon dioxide formed in the oxidation zone depends on the oxygen partial pressure and the temperature. If excess oxygen is present, some of the carbon monoxide will be converted to CO₂ by gas phase oxidation.

In addition, in entrained-bed gasifiers and some fluidized-bed gasifiers where devolatilization occurs in an oxygen-rich environment, tars and oils and other organics are also oxidized in the gas phase, forming carbon monoxide, carbon dioxide, and hydrogen.

Water-Gas Shift

An important gas-phase reaction occurring in the gasifier involves the equilibrium among carbon monoxide, carbon dioxide, hydrogen, and water vapor:



The composition of the raw product leaving the gasifier is significantly influenced by this equilibrium. High temperature favors the formation of

carbon monoxide and water vapor. The relative partial pressures of the various reactants also influence the equilibrium composition.

Sulfur and Nitrogen Reactions

Coal contains varying amounts of sulfur and nitrogen. Significant reaction products formed from these elements during gasification include ammonia, hydrogen cyanide, hydrogen sulfide, carbonyl sulfide, and other organic sulfur species (such as mercaptans). The quantities of such species formed depend on a number of factors including coal sulfur and nitrogen content, temperature, pressure, and hydrogen concentration in the gas. The ratio of carbonyl sulfide to hydrogen sulfide is a particularly important concern because this ratio can affect the selection, design, and performance of downstream acid gas removal and sulfur recovery processes. As with the water-gas shift reactions discussed above, the ratio of COS to H₂S in the raw gas is affected by the steam and carbon dioxide content of the gas due to the chemical equilibrium which is maintained at high temperatures among these four species:



Similar relationships may also hold for nitrogen species such as ammonia and hydrogen cyanide.

Solid Waste

Coal contains substantial quantities of nonreactive mineral matter which remains after the coal has been gasified. The resulting solid waste will be in the form of ash or solidified slag droplets, depending primarily on the reactor operating temperature and the ash fusion point. Fixed-bed gasifiers can be operated to produce either a "dry", unfused ash (low-temperature operation) or a fused slag by-product (high-temperature operation). Entrained-bed gasifiers operate at high temperatures and produce a slag

by-product. Some fluidized-bed gasifiers operate at a temperature at which the ash particles are soft and sticky and form agglomerates that are removed from the gasifier. Some of the mineral matter components may also be volatilized; the extent to which this occurs depends on the temperature and the chemical forms in which these compounds are found in the coal.

The susceptibility to leaching of the species remaining in the ash or slag also varies depending on their solubility and the ease with which water can penetrate the solid. For example, fused slags are less amenable to leaching than more porous ash particles.

Figure 1 shows the conceptual zones into which fixed-bed and fluidized-bed, and entrained-bed gasifiers may be divided. Note that in the fixed-bed gasifier and fluidized-bed gasifiers, the relative direction of gas and solid flows is countercurrent, while it is co-current in the entrained-bed gasifier. Also note the differences in the order of the various reaction zones.

Associated closely with the gasification operation are the equipment and operations required to prepare the coal and feed it into the gasifier vessels. In the case of most small, low-Btu gasification facilities, very limited coal preparation is performed. These facilities typically gasify coal which has been sized prior to its delivery to the site. Some screening of the coal for removal of fines is performed at two of the low-Btu facilities tested (Wellman-Galusha of Fort Snelling, and Foster-Wheeler/STOIC at UMD). As-received coal is crushed and sized on site at the medium-Btu facilities considered in this report. At the Kosovo (Lurgi-type), KRW PDU, Koppers-Totzek (Modderfontein and Ptolemais) facilities, coal drying is performed. The entrained-bed gasifiers (Koppers-Totzek and Texaco) require more extensive preparation (crushing and pulverizing) to produce the finely divided coal feed used in these gasifiers.

A variety of methods are used to feed the prepared coal into the gasifiers. Lockhoppers are used with Wellman-Galusha, Riley, Foster-Wheeler/STOIC,

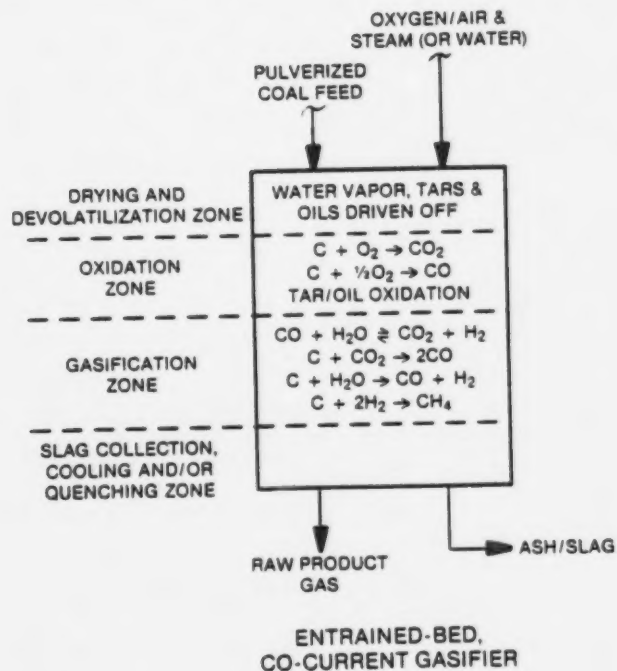
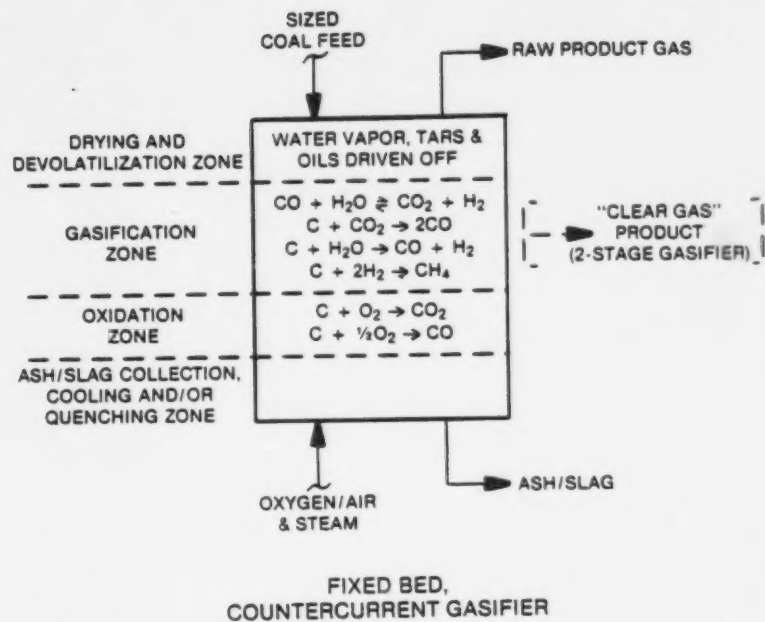


Figure 1. Conceptual configurations of different gasifier bed types.

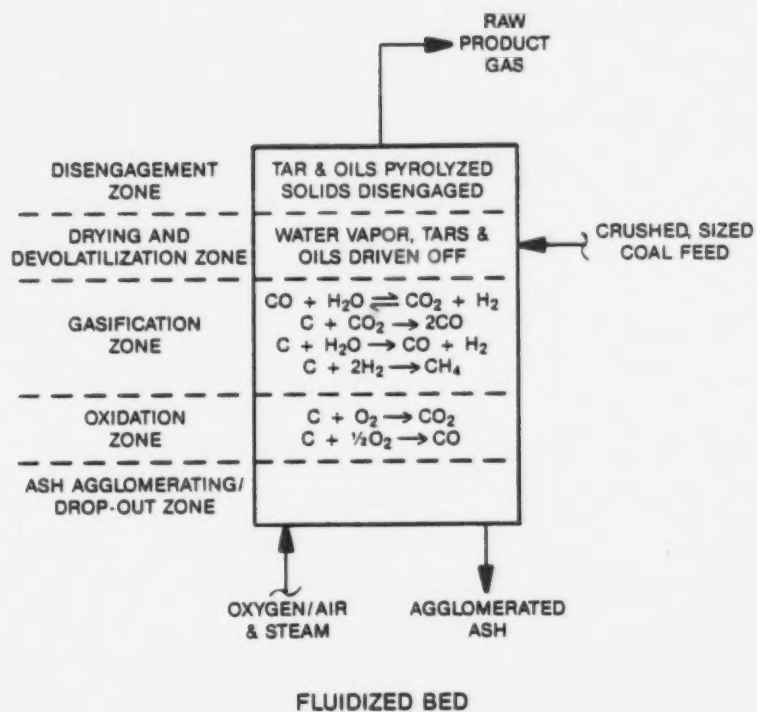


Figure 1. (Continued)

Lurgi and KRW gasifiers. At the Chapman gasifier facility, coal is fed by means of a rotating feeder known as a barrel valve. In the Koppers-Totzek gasifier, coal is augered out of a storage vessel and transported to the gasifier in a heated stream of steam and oxygen using a screw conveyor. The Texaco gasifier utilizes slurry feeding in which pulverized coal is mixed with water, preheated, and pumped into the gasifier vessel.

Figures 2 through 4 summarize coal composition, gasifier feed rates, and reactant ratios for each of the eight gasification facilities. Flow rates are shown on a "per gasifier" basis to facilitate comparisons. The reactant ratios were calculated based on the reported feed rates. For the air-blown gasifiers, the oxygen to coal ratio was calculated based on an oxygen content of 23.1 percent by weight for air.

SUMMARY AND COMPARISON OF DOWNSTREAM PROCESSING OPERATIONS

Processing operations downstream of gasification are needed to perform various functions including:

- Removal of entrained particulates (fly ash, tar, oil, etc.);
- Removal of gaseous contaminants (primarily sulfur and nitrogen species);
- Cooling of the raw product gas;
- Handling and disposal of solid wastes;
- Treatment and disposal of wastewater;
- Recovery of by-products (e.g., sulfur, ammonia, organics);
- Control of air pollutants; and
- Upgrading of the raw gas.

All of these processing operations are not present in all gasification facilities. Those found in the gasification facilities included in this

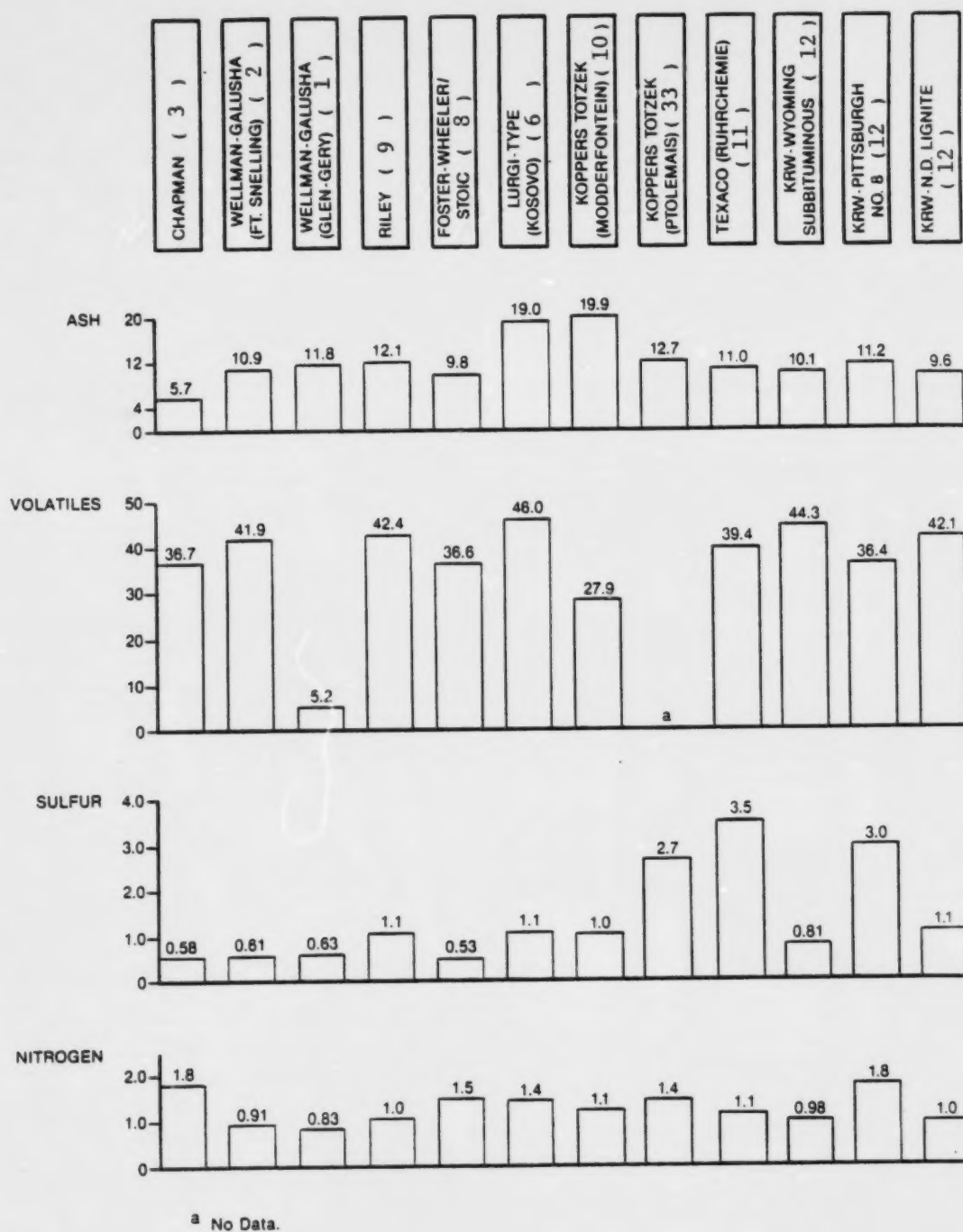
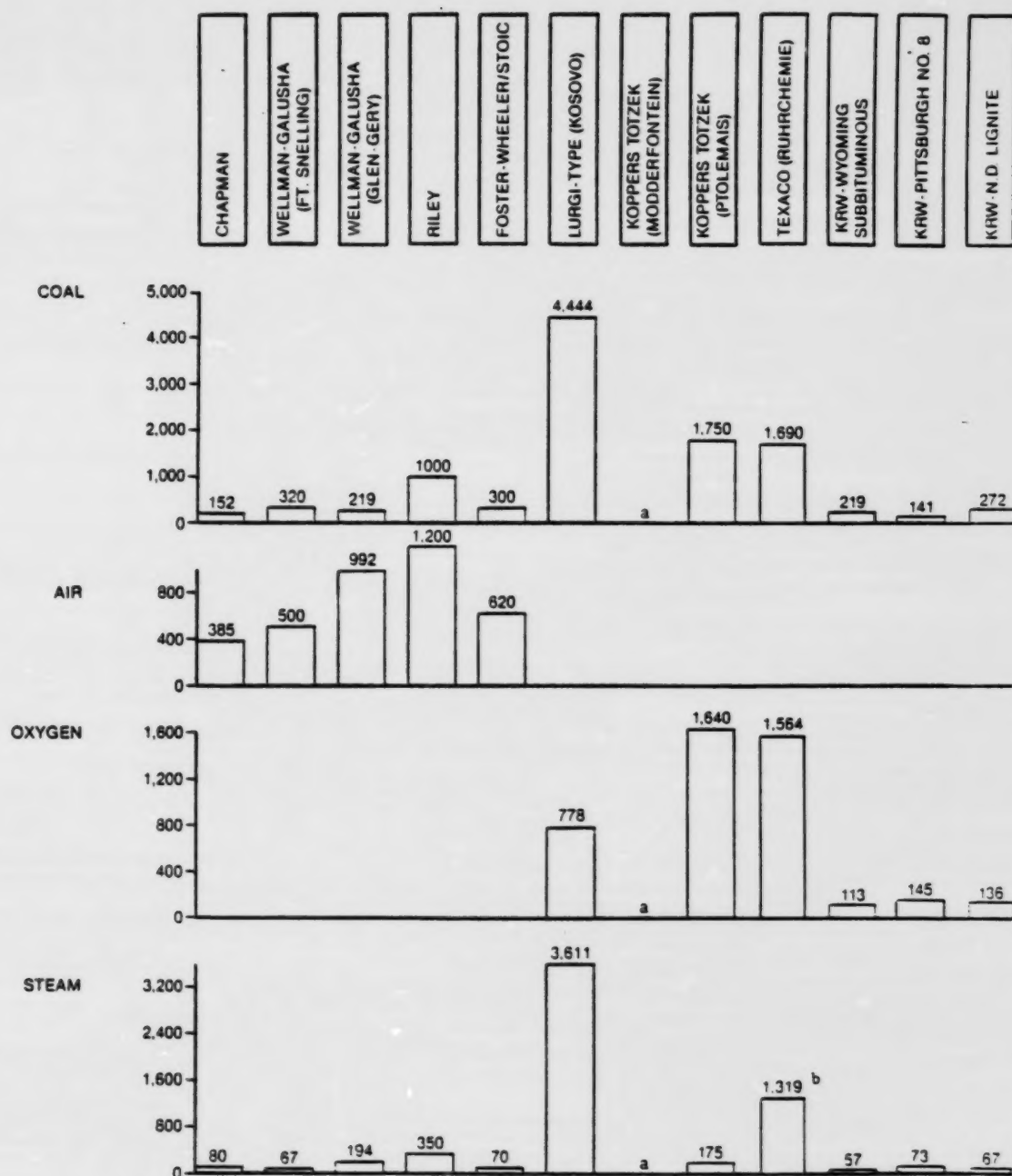


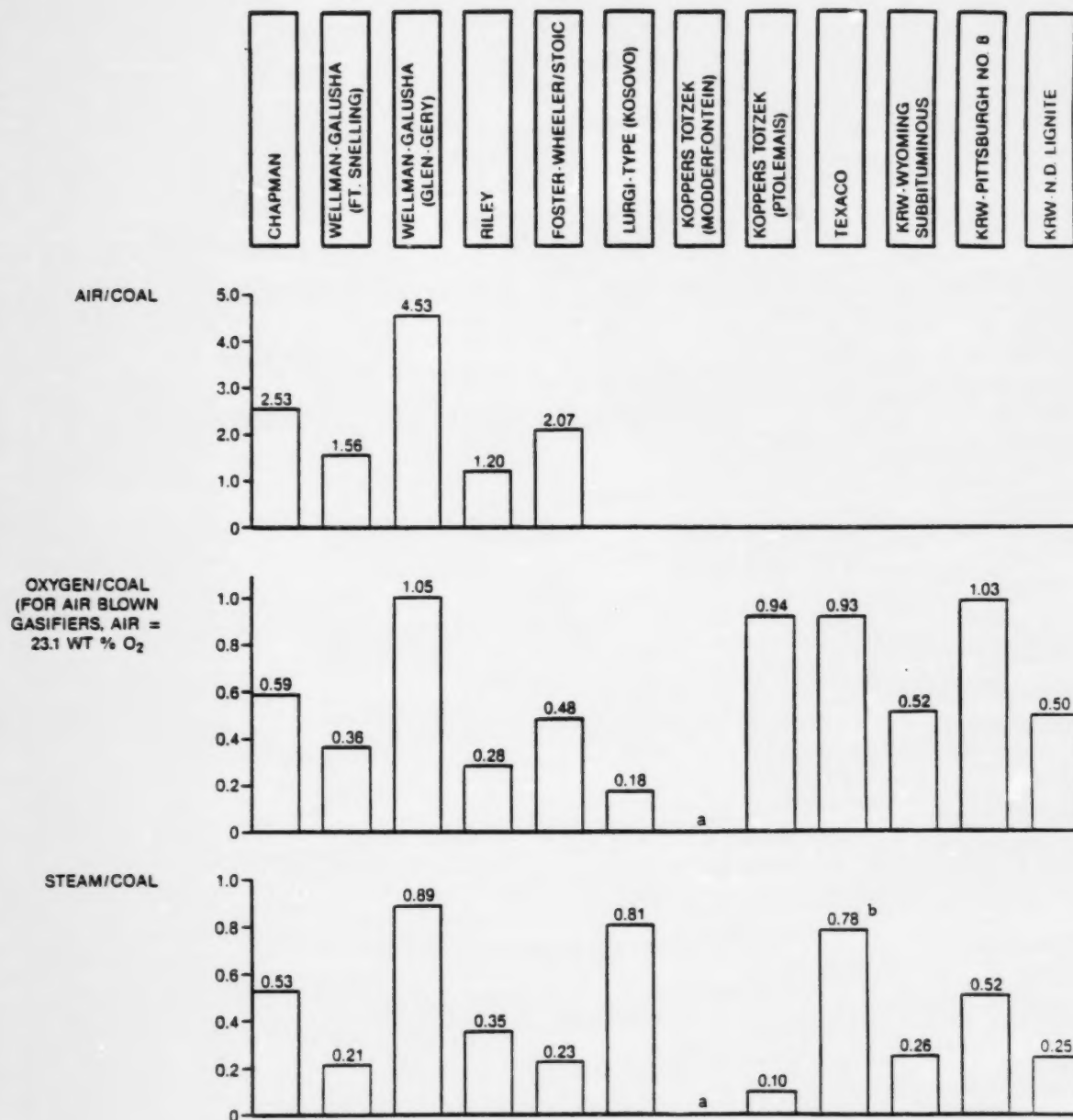
Figure 2. Comparative coal feedstock analyses, dry basis, wt %.



^aNo data available.

^bFor the Texaco Gasifier Only, the Steam Flow Rate is Taken as the Fresh Makeup Slurry Water, Coal Moisture, and Water in Additive and Flocculant.

Figure 3. Comparative gasifier feed rates, g/sec-gasifier.



^aNo data available.

^bFor the Texaco Gasifier Only, the Steam Flow Rate is Taken as the Fresh Makeup Slurry Water, Coal Moisture, and Water in Additive and Flocculant.

Figure 4. Comparative gasifier feed ratios, kg/kg.

report were shown in Table 1. Figures 5 through 14 are simplified block flow diagrams of these facilities. The major processing units and streams present in each of the facilities are shown, together with stream temperature data obtained at the time the facilities were characterized. Those streams for which composition and/or flow rate data were obtained are also indicated. These diagrams clearly show similarities and differences among the facilities.

In general, the low-Btu gasification facilities have much less extensive downstream processing than the larger, more complex medium-Btu facilities. In addition, since the emphasis at the KRW PDU is on gasifier development, limited gas cleaning is practiced. In several of the low-Btu facilities, gas cleanup consists only of removing some entrained particulates, typically by the use of cyclone separators. This is particularly true of the facilities which produce a hot fuel gas for direct combustion of a process furnace. The Foster-Wheeler/STOIC facility (which features two-stage gasification) utilizes an electrostatic precipitator (ESP) to remove oil and tar particulates from the top gas and a cyclone to remove dust from the bottom gas. Of the low-Btu gasifiers tested, only the Chapman facility utilizes wet scrubbing and produces a cooled fuel gas, by-product tars and oils, and process condensate (wastewater) stream. Some type of wet scrubbing is used in all of the medium-Btu facilities. None of the low-Btu facilities have acid gas removal systems; all of the medium-Btu facilities have such units.

Ash/slag removal techniques also vary. All of the facilities except the KRW PDU use water to quench the hot ash/slag or to facilitate its removal from the gasifier vessel by sluicing. The pressurized gasifiers (Lurgi, KRW, and Texaco) all utilize lock hoppers to remove ash/slag. The others utilize ash plows, mechanical conveyors, or slide valves.

The downstream processing operations can significantly influence the fates of the various solid, liquid, and gaseous pollutants generated in the gasifier. Components originally found in the raw gas may be removed by these

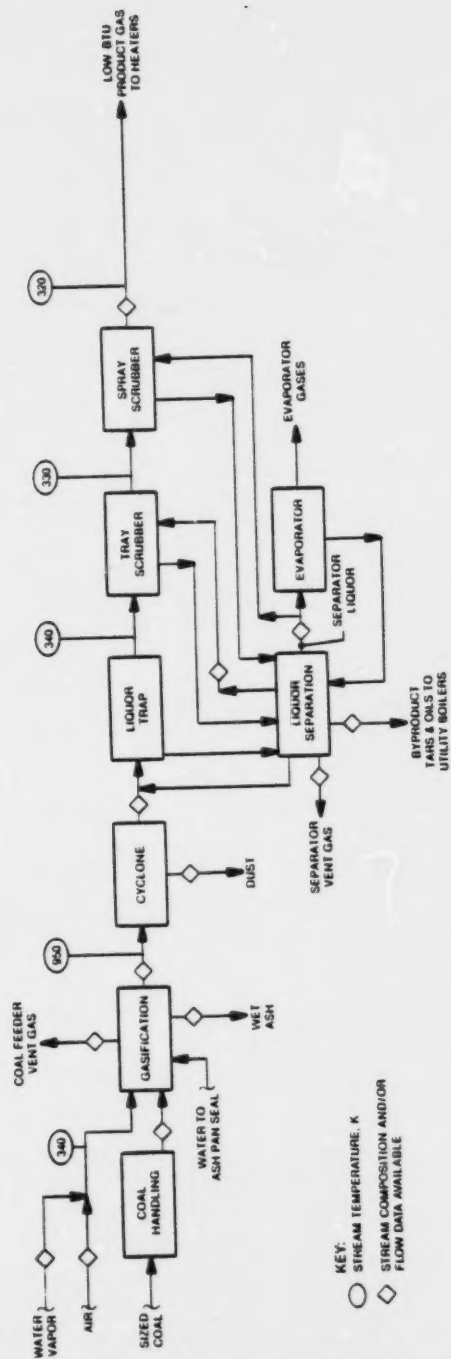


Figure 5. Simplified block flow diagram of Chapman gasifier.

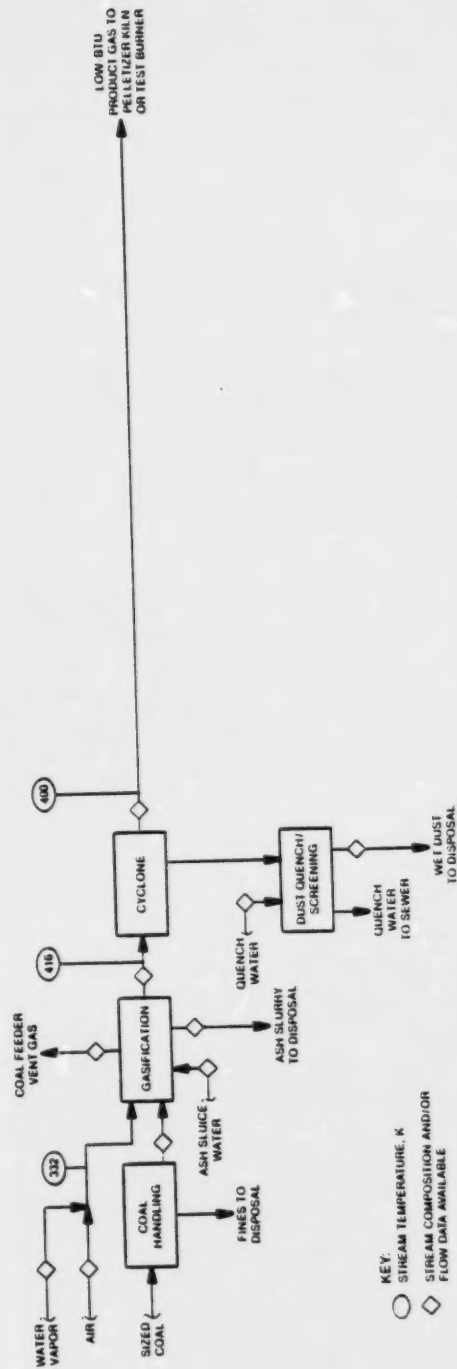


Figure 6. Simplified block flow diagram of Wellman-Galusha (Ft. Snelling) gasifier.

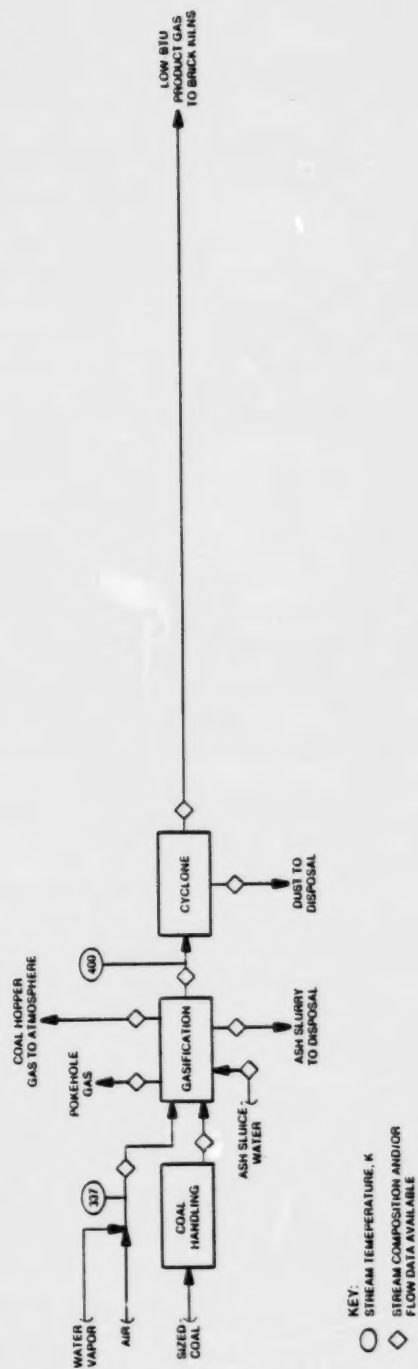


Figure 7. Simplified block flow diagram of Wellman-Galusha (Glen-Gery) gasifier.

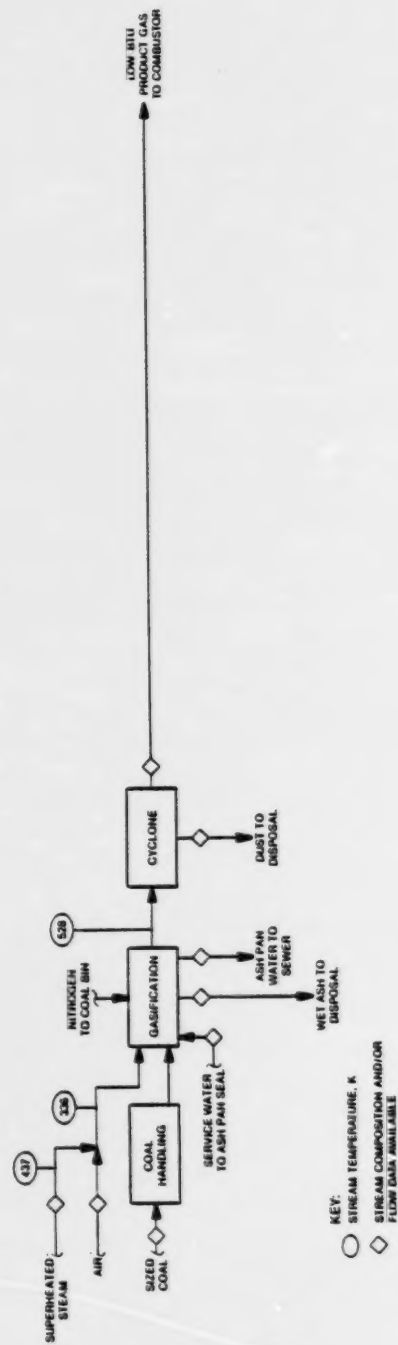


Figure 8. Simplified block flow diagram of Riley gasifier.

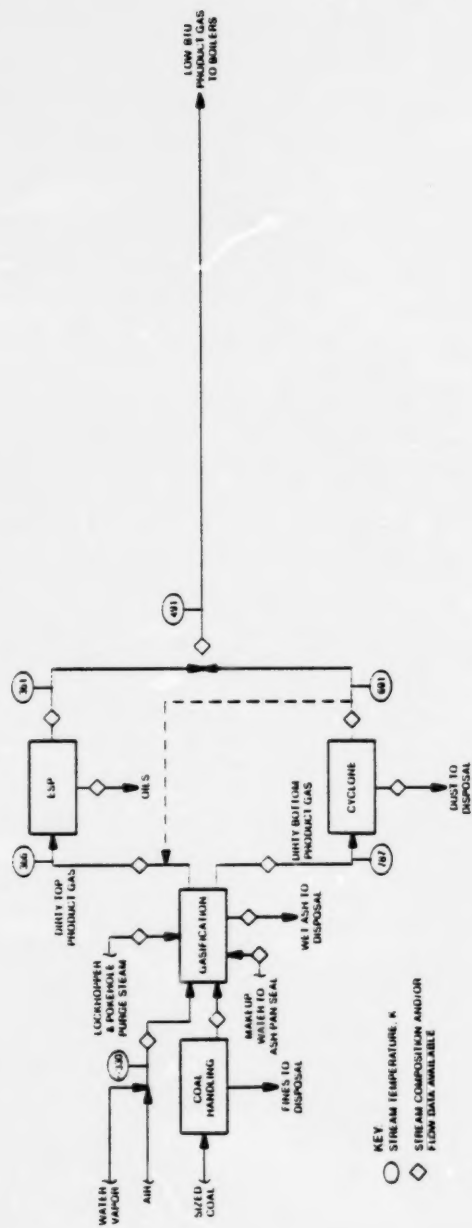


Figure 9. Simplified block flow diagram of Foster-Wheeler/STOIC gasifier.

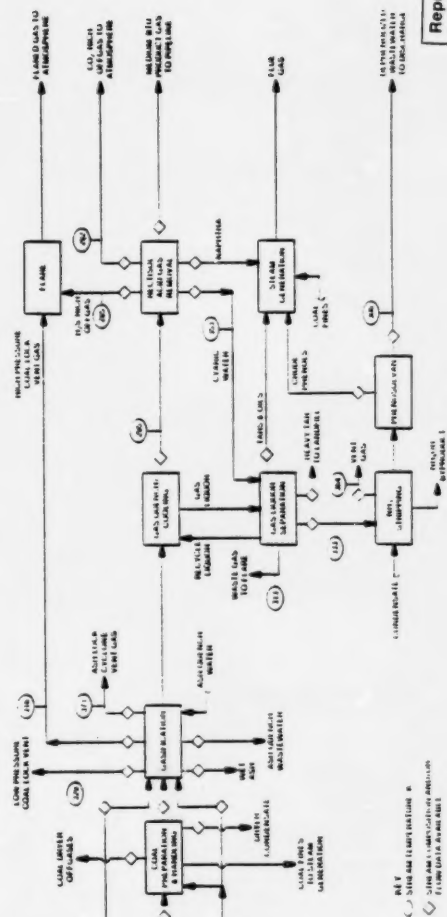


Figure 10. Simplified block flow diagram of Lurgi-type gasifier.

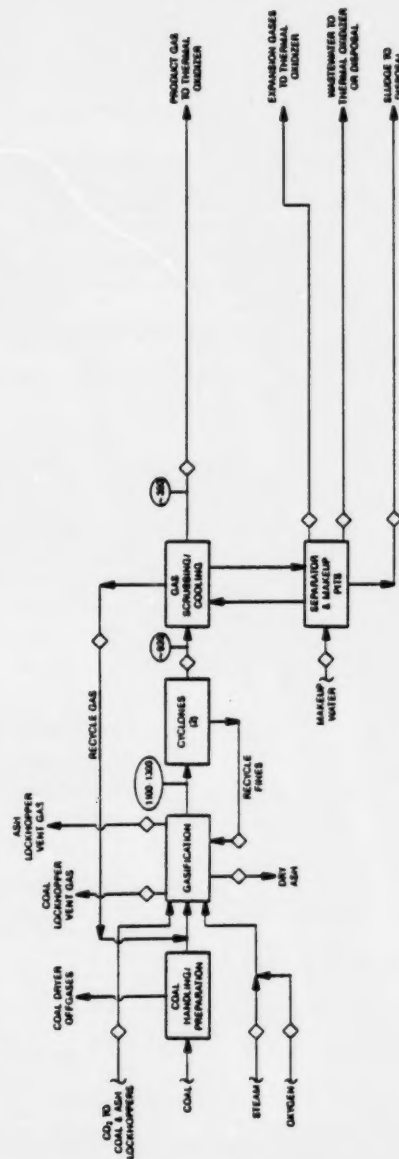


Figure 11. Simplified block flow diagram of KRW PDU gasifier.

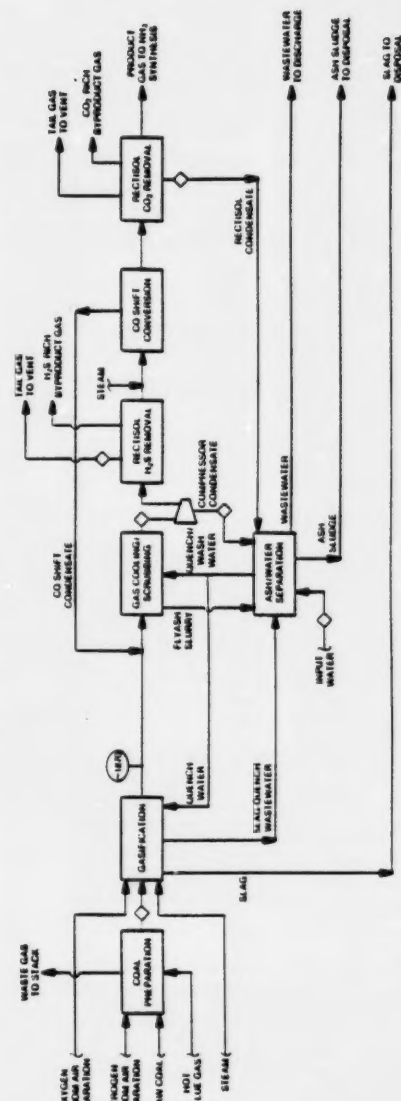


Figure 12. Simplified block flow diagram of Koppers-Totzek (Modderfontein) gasifier.

operations and distributed in a number of secondary solid, liquid or gaseous streams. This distribution depends on the way in which these processes are linked together, how they are designed and operated, and on stream compositions.

Flow rate data for the major streams entering and leaving the downstream processing units for each of the facilities considered are summarized in Appendix A.

SECTION 4

WASTEWATER CHARACTERIZATION DATA SUMMARY

INTRODUCTION

Wastewater characterization data on the aqueous wastes from both fixed-bed and entrained-bed commercial coal gasification processes were gathered from numerous source test and evaluation studies at synthetic fuels facilities in order to identify environmental and health issues requiring further definition. These gasification facilities are the Wellman-Galusha (Glen Gery), Wellman-Galusha (Fort Snelling), Chapman-Wilputte, Lurgi (Westfield, Scotland), Lurgi-type (Kosovo), Lurgi (Sasolburg), Foster Wheeler/STOIC, Riley Gas Producer, Koppers-Totzek, and Texaco processes (1,2,3,4,5,6,7,8,9,10,11). Information regarding the test period and coals gasified is presented in Table 2. The results of wastewater characterization studies performed on the KRW-PDU are also included for comparison with the Koppers-Totzek and Texaco entrained-bed gasifiers because the quench condensates from this ash-agglomerating gasifier have similar chemistries (12).

The environmentally significant species evolved from coal during gasification in low- and medium-BTU processes can be broadly grouped into five categories: heavy hydrocarbons (C_6^+ , oils, and tars), volatile nonmethane hydrocarbons (C_2-C_5), inorganic sulfur compounds, inorganic nitrogen compounds, and trace elements. The process areas that generate wastewaters with these contaminants are coal preparation, coal pretreatment (thermal drying, mild oxidation, slurry preparation), coal gasification, particulate removal and gas cooling, shift conversion, and acid-gas removal. Wastewaters from these process areas contain some or all of the categories of pollutants

TABLE 2. COAL AND COAL GASIFICATION FACILITY TYPE

Type of Gasifier	Site	Type of Coal	Year of Study	Product Gas Heat Content ^a
Chapman-Wilputte	Kingsport, Tennessee	Virginia bituminous	1978	low
Foster Wheeler/STOIC	U. of Minnesota Duluth	Bituminous coal from Pinnacle Seam	1981	low
Koppers-Totzek	Modderfontein, So. Africa	Bituminous, high volatile coal from So. Africa	1979	medium
Lurgi, Dry Ash	Westfield, Scotland	Rosebud, sub-bituminous coal from Montana; Bituminous coals from Percy, Illinois; and Pittsburgh non-caking and non-swelling coal from Federal No. 1 mine	1973-1974	medium
Lurgi-type, Dry Ash	Kosovo, Yugoslavia	Lignite from Kosovo mine	1981	medium
Lurgi, Tri-State Synfuels Test	Senoilburg, So. Africa	Western Kentucky coal	1981	medium
Biley (modification of Morgan Gas Producer)	Worcester, Massachusetts	North Dakota lignite	1979	low
KRW-PDU	Madison, Pennsylvania	Wyoming sub-bituminous, Pittsburgh #8 bituminous, and North Dakota lignite	1983	medium
Texaco	Buhrkohlle/Suhrchemie Federal Republic of Germany	Illinois bituminous	1980	medium
Wellman-Galusha	Glen-Gery Brick Co. York, PA. Fort Snelling	Pennsylvania anthracite North Dakota lignite (Indianhead)	1978 1978	low low

^aLow means less than 5500 kilojoules per cubic meter; medium means approximately 11,000 kilojoules per cubic meter.

identified above. This report will evaluate characterization data for wastewaters produced during coal gasification, particulate removal and gas cooling, and acid-gas removal.

MAJOR POLLUTANTS

Heavy Hydrocarbons

Most of the heavy hydrocarbons, if produced, are condensed from the raw product gas and appear in a hydrocarbon condensate. Due to the contact of this condensate with condensed steam or recycled quench water, a portion of the total mass of each hydrocarbon will also appear in the aqueous condensate. The amount will depend on the solubility of the compound in water and the transfer efficiency of the solid-liquid contact.

Light Hydrocarbons

Light hydrocarbons will mostly appear in the off-gases from acid-gas removal and the product gas. Due to their low solubilities in water, minor quantities would be expected to appear in the aqueous and hydrocarbon condensates.

Inorganic Sulfur

Inorganic sulfur (as distinguished from sulfur in the heavy hydrocarbons) consists mainly of hydrogen sulfide, carbonyl sulfide, and other reduced sulfur compounds. The majority of these compounds ultimately appear in the off-gases from acid-gas removal. However, as the inorganic sulfur compound with the highest solubility, a portion of the H_2S probably partitions during gas cooling to the aqueous quench condensate.

Inorganic Nitrogen

Inorganic nitrogen (exclusive of nitrogen present in the heavy hydrocarbons) consists mainly of ammonia and smaller amounts of hydrogen cyanide. In contrast to the sulfur species, the bulk of the ammonia appears in the aqueous quench condensate, and only traces appear in the acid-gas removal off-gases and blowdowns. This is due to ammonia's high solubility in water. Hydrogen cyanide is also soluble in water, but its capture is influenced by the pH of the quench water. Therefore, removal of hydrogen cyanide in the raw product gas quench system will vary with quench operation.

Trace Elements

It is anticipated that with the exception of mercury, the majority of the trace elements generated from the gasification of coal will appear in either liquid or solid process wastes. Solid wastes typically include the gasifier ash, overhead particulate, and various spent catalysts. Liquid effluents include water in contact with these solids (e.g., coal pile runoff, solid waste leachates, and ash/particulate sluice water) as well as the aqueous quench condensate and acid-gas removal blowdowns.

DEFINITION OF AQUEOUS WASTE STREAMS

The aqueous waste streams examined during the source test and evaluation studies are of two types: contaminated process area wastewaters produced during coal preparation, coal gasification, particulate removal, gas cooling, and acid-gas removal, and leachate drainage from solid waste storage.

Contaminated Process Area Wastewaters

The nature and type of the process area wastewaters vary with the coal gasification process and the extent of downstream processing. In low-BTU

facilities where gas cleanup consists only of removing entrained particulates with cyclone separators or electrostatic precipitators, the principal wastewater is produced during ash quenching in the ash pan. In medium-BTU facilities, wet scrubbing is used to quench the product gas before acid-gas removal. All the included gasification facilities use water to quench hot ash or slag and to facilitate its removal from the process area by sluicing.

Ash Pan Water--

The Riley and Foster-Wheeler/STOIC gasifiers quench the ash produced by the process in a water-filled ash pan below the gasifier, which also forms a water seal for the gasifier. The ash pan rotates constantly and forces ash into buckets situated at the bottom of the ash pan. Hydraulically operated buckets lift the ash from the ash pan and drop the ash onto a belt conveyor which transfers the ash to a storage location prior to disposal. The system requires makeup water for maintenance of the ash pan water level. Water losses from the ash pan are due to evaporation and carryover with gasifier ash. Ash pan carryover water is the only process blowdown from this gasifier. Although this blowdown is intermittent and of a relatively small volume, it may contain elevated concentrations of trace elements and conventional pollutants.

For the Lurgi gasifier, hot ash generated during gasification is collected from the bottom of the gasifier in a lock hopper. This ash is water quenched and discharged to a landfill. At the Kosovo facility, the resultant aqueous blowdown (quenched ash water) is combined with the coal bunker scrubber blowdown and discharged. In the Wellman-Galusha (Fort Snelling) gasifier, water quenches cyclone dust produced by a refractory-lined cyclone used for particulate removal from the product gas. The cyclone dust quench water is then separated from the particulates and discharged. A similar wastewater produced by the Texaco process is the slag water that is used to quench the coarse and fine slag produced during gasification. In this process, coal ash forms a slag which is quenched with recycled water. The slag is blown down periodically through a lock hopper that is flushed with process water. Coarse

slag is separated from the fine slag and water by screening. The slag water is eventually decanted from the fine slag and sent to the process sewer. A unique aspect of the Texaco process is that the slag quench water is also in intimate contact with the product gas. A different water is used to sluice the slag from the lock hopper.

Ash Sluice Water--

Both the Glen-Gery and Fort Snelling Wellman-Galusha gasifiers remove ash through a grate where it accumulates in a hopper at the bottom of the gasifier. Ash is normally dumped from this hopper several times a day. During ash removal, water is added to the ash hopper to seal the gasifier from the atmosphere and to slurry the ash to aid in its removal. The ash slurry is sluiced (flushed) from the hopper and transported to a disposal area. Decanted sluice water is returned to the gasifier for reuse. Low volume blowdowns occur periodically from the system; however, this is not a major wastewater source.

Coal Slurry Water--

At some Lurgi facilities coal is dry-screened to remove coal particles smaller than those allowed in the gasifier. The collected coal fines are slurried and sluiced to a decant tank where they are separated from the slurry water. At the Lurgi Sasolburg facility, the clarified slurry water is used as makeup to the gasifier and power station ash sluicing systems. Since wet coal screening is likely to be required at most commercial fixed-bed coal gasification facilities, coal slurry water blowdown is a probable aqueous waste requiring disposal. Periodic blowdowns are required from a coal screening water loop in order to reduce scale accumulation in various portions of the system. This stream contains coal fines and other suspended matter as well as dissolved solids leached from the coal. In order to minimize the wastewater discharge from the coal screening system, a large portion of the slurry water must be recycled. Recycle of this stream will require that the chemistry of the makeup and recirculating water be controlled to avoid operating problems due to scaling or corrosion.

Quench Condensates--

Quench condensate is the principal wastewater produced from coal gasification facilities that use wet scrubbing of raw product gases. This stream is important in wastewater treatment design because it represents the largest and most contaminated aqueous stream from gasification processes. Typical quench condensates are the gas liquor (Lurgi), separator liquor (Chapman), the settler underflow (also called excess water blowdown) from the Texaco quench system, and quench liquor from the KRW-PDU. The Koppers-Totzek gasifier also has a characteristic quench condensate that is similar to the Texaco settler underflow wastewater (13).

Quench condensates contain several different categories of pollutants. These are dissolved organics (mainly a fixed-bed process concern), dissolved inorganic gases, suspended solids, and dissolved inorganics. The complex composition of the quench condensates dictates that multiple treatments are required for upgrade. For the Lurgi process, raw gas liquor (RGL) as described in this report is a quench condensate after tar and oil separation. Extracted gas liquor (EGL) and Phenosolvan water or effluent represents the effluent from a solvent extraction treatment process that removes a large percentage of phenolic compounds present in fixed-bed gasifier wastewaters. Phenosolvan effluent is then steam stripped to remove dissolved gases such as ammonia, hydrogen cyanide, and hydrogen sulfide. The stripped gas liquor (SGL) analysis represents the steam stripper effluent. This stream is diluted (as compared to RGL and EGL) because of condensation of steam during the stripping process.

Gas quenching and scrubbing in the Chapman process consists of removing tars and oils from the hot gas and cooling the gas with in-line sprays followed by spray scrubbers. Tar-laden quench liquor is sent to a tar/oil separator where the tars settle and oil is removed from the surface. The quench liquor is cooled and recycled to the gas quenching and scrubbing processes. Within this system, quench condensates are reused many times

before being blown down to wastewater treatment. The system is operated to minimize the quantity of separator liquor sent to wastewater treatment.

In the Texaco process, the raw gas is cooled by indirect heat exchange (waste heat boiler) and/or by direct quenching. The method of cooling is determined according to the end use of the gas. The quenched and cooled gas is scrubbed in a water scrubbing system that removes entrained particulates from the gas. Water from various process sources, such as the quenching zone of the gasifier, the scrubber, and the slag sluicing system, are combined in a settler/clarifier. Clarified water is recycled to the process while the underflow water containing solids is recycled to the coal slurry system. A blowdown stream from the settler/clarifier is removed to prevent the buildup of soluble species in the system. This blowdown is called either settler underflow or excess water, and removal of solids could be accomplished by filtration.

In the Koppers-Totzek process, hot raw gas from the waste heat boiler is cooled and scrubbed of entrained dust in two stages. The first stage consists of a washer cooler which reduces the gas temperature and provides bulk dust removal by means of direct water scrubbing. Additional cooling and dust removal are subsequently achieved in Thiesen disintegrators and droplet separators. Final dedusting is provided by a wet electrostatic precipitator (13). Quench condensates collected in the washer cooler, droplet separator, and wet electrostatic precipitator are combined in a settling basin designed to remove suspended solids so that decanted liquor can be recycled back to the process. Existing Koppers-Totzek gasification facilities utilize cooling towers for wash water cooling; however, commercial designs for U.S. facilities feature indirect cooling to eliminate the potential for volatilization of pollutants such as NH_3 and HCN (13). The settler underflow is filtered to produce dewatered dust and filtrate which is combined with a portion of the clarifier overflow as blowdown for control of dissolved component buildup. The resultant aqueous waste stream is the principal wastewater source from the Koppers-Totzek gasifier. Source test data on this stream are not available

for the Modderfontein facility. However, limited conventional pollutant analytical data are available for quench condensates produced during the TVA tests at Ptolemais, Greece (see Section 6.0).

The quench condensate from the KRW-PDU is produced during cooling of the raw product gas. After leaving a cyclone, the raw product gas is quenched in a quench scrubber, then further cooled and scrubbed with water in a packed-bed cooler (product gas cooler). Most of this gas is routed to a thermal oxidizer. A portion of the gas is further scrubbed and cooled in a second packed-bed gas cooler before being recycled back to the gasifier. Scrubber and cooler waters are also recycled. The water blowdown from each of these units is depressurized and routed to a separator pit, where solids are removed. Waters from the separator are returned to the quench unit and coolers, and excess water is routed to wastewater storage tanks (and subsequently disposed off site).

Gas Compression and Cooling Condensates--

Koppers-Totzek technology involves coal gasification at atmospheric pressure. However, downstream unit operations (particularly in the case of physical absorption processes) are more efficient and economical at elevated pressures. Therefore, the raw gas is compressed prior to subsequent treatment. The temperature rise of the gas during compression is controlled by coolers which produce a condensate stream (compressor condensate). Characterization data for raw gas compression and cooling condensate for the Koppers-Totzek gasification facility at Modderfontein relate to the gasification of South African sub-bituminous coal and are likely to be coal specific.

Acid Gas Removal Wastewater--

Although many acid gas removal systems do not generate a contaminated wastewater, the Rectisol process is an exception. Rectisol is an acid gas removal process that removes CO_2 , H_2S , COS , HCN , NH_3 , organic sulfur compounds, benzene, and gum-forming hydrocarbons from synthesis gases by means of physical absorption in cold methanol. Characterization data for aqueous

wastes from the Rectisol process are available for the Lurgi-type Kosovo (cyanic water) and the Koppers-Totzek Modderfontein (Rectisol condensate/still bottoms) facilities (6,10). This liquid waste stream is generated from the methanol/water distillation column. At the Lurgi-type facility, this stream is combined with aqueous condensates from an organics (naphtha) separator. At the Modderfontein facility, a water-based pre-wash is used to remove ammonia and hydrogen cyanide before the gas enters Rectisol. This cyanide wash water is combined with wastewaters from gas cooling and dust removal and raw gas compression and cooling processes and sent to wastewater treatment.

Other acid gas removal processes are absorption with alkanolamines, dimethyl ether of polyethylene glycol, and hot potassium carbonate. The alkanolamines are the most widely used solvents for removal of acid gases from gas streams. The two amines that have seen extensive commercial use in gas purification are monoethanolamine (MEA) and diethanolamine (DEA). Diisopropanolamine (DIPA) and methyldiethanolamine (MDEA) are also used because of their selectivity for H_2S in the presence of CO_2 . The reaction of amines with gas contaminants lead to chemical degradation of the amine solutions and the subsequent generation of wastes. In the MEA or DEA process, degradation products are removed by filtration of the recirculated amine solution. The waste generated is a filter residue containing iron sulfide (a corrosion product), liquid hydrocarbons, and MEA or DEA degradation products. In some processes, degradation products are removed by blowdown of the recirculating amine solution. This waste stream will also contain trapped impurities, hydrocarbons, and corrosion products.

The technology that uses dimethyl ether of polyethylene glycol (DMPEG) for removal of H_2S , CO_2 , COS, CS_2 , and mercaptans from gas streams is the Selexol process. A spent solvent is not generated from the Selexol process because degradation of the DMPEG does not occur. However, a sour condensate may be generated from the regeneration of the Selexol solvent, depending on the water content of the feed gas and the specific design of the process. This sour condensate may contain carbon dioxide, methane, hydrogen sulfide, and carbonyl sulfide.

The standard Benfield process uses a hot potassium carbonate solution containing additives, corrosion inhibitors, and activators to chemically absorb CO_2 and H_2S from gas streams. Chemical losses may occur due to the loss of absorption solution through leaks, upsets, and surplus water discharges. When the CO content of the feed gas is high or at high temperature, CO will react with K_2CO_3 to form potassium formate. A purge of solution is necessary to remove the formate and fresh carbonate solution makeup is required.

Leachate Drainage

Coal gasification processes generate solid wastes with widely divergent characteristics that are dependent on gasifier type and operation and the nature of the coal feed. Ash from a gasifier that operates at a temperature below the ash fusion point is composed of loose agglomerates of small particles that break readily into discrete particles. Ash from a gasifier that operates at a temperature above the ash fusion temperature is discharged from the reactor as a melt. During subsequent water quenching the melt shatters into discrete particles.

Leachates from the storage of gasifier solids in a disposal site may be composed of the liquid bound with the solids transported to the disposal site together with seepages of groundwater through the site and drainage from precipitation. If the solids are in direct contact with the soil, percolation of leachate into the soil and eventual movement to groundwater is also possible. If the soil at the disposal site is relatively impervious or the quantity of leachate is large, either continuously or intermittently, runoff from the site may lead to surface water contamination. Therefore, the characteristics of the leachates from gasification slag and ash are of interest.

The type of gasification solids examined during the source tests were ash from the Lurgi-type, Wellman-Galusha, and Chapman gasifiers; cyclone dust from the Chapman and Wellman-Galusha gasifiers; spent filter media from the Lurgi-

type tar/oil separation system; and fine and coarse slag from the Texaco process. Solids collected from the processes were subjected to two separate leaching procedures: the American Society for Testing and Materials (ASTM) and the Resource Conservation and Recovery Act-Extraction Procedure (RCRA-EP).

WASTEWATER CHARACTERISTICS

Data for the wastewater characteristics of a number of coal gasification processes are summarized in this section. Wastewater data are cataloged by conventional pollutants (e.g., BOD, COD, NH_3 , TDS), trace elements, and organics for both fixed-bed and entrained flow gasifiers. Three wastewater categories were evaluated: process wastewaters from coal gasification, particulate removal and gas cooling, and acid gas removal; process wastewaters from ash and slag handling; and leachates from gasification slag and ash.

Wastewaters From Coal Gasification Processes

Conventional Pollutants--

The conventional pollutant concentrations found in wastewaters generated from the Riley, Chapman, Wellman-Galusha, Koppers-Totzek, and KRW-PDU gasifiers are presented in Table 3. Data for conventional pollutants in Lurgi and Lurgi-type process wastewaters are presented in Table 4 for both raw and pretreated gas liquors and acid gas removal blowdowns. These data indicate that quench condensates produce the most contaminated waste streams from coal gasification. The apparent chemical oxygen demands for typical fixed-bed gasifier gas liquors are between 8000 and 22,000 mg/L. These liquors also contain substantial amounts of BOD, NH_3 , SCN, CN, reduced sulfur compounds, and carbonates. The waters have high apparent buffer capacities and contain high dissolved solids. The Lurgi gas liquors contain significant quantities of both dissolved organics and volatile inorganics. Some data discrepancies exist (e.g., chloride levels in raw and treated gas liquors from Sasolburg); however, the overall characteristics of the quench condensates are in good agreement with regard to the pollutant matrix for the waters.

TABLE 3. CONVENTIONAL POLLUTANTS IN COAL GASIFICATION WASTEWATERS^a

Gasification System	Riley	Chapman	Wellman-Galusha at Fort Snelling	Koppers-Totzek at Modderfontein	KRM-PDU				
Type of Wastewater	Ash Pan	Separator Liquor	Cyclone Dust Quench Water	Com-pressor Con- densate ^c Rectisol ^b Rectisol ^c	Sub-bituminous Bituminous Lignite				
pH, standard units	11.3	7.66	10.0	8.2	8.0	8.1	8.4	8.4	8.7
TDS	2,460	6,300	390	260	170	1,390	1,640	390	2,249
TSS	32	144	d	<1	12	70	20	4600	1,000
Hardness as CaCO ₃				60	46	691	554		
Alkalinity as CaCO ₃		2,140		2,990	2,690	78	144	6770	2382
Conductivity (umho/cm)	2,900	32,000		6,000	5,500	1,800	2,000	12,300	5,200
COD	87	22,200	800	644	569	28	1,000	150	237
TOC	15		185					48	55
BOD	44	6,530	85						170
NH ₃ (Total)		5,000	0.97	973	900	26	49	2,430	965
CM ^e	ND ^e	1,000	0.36	7.3	10.5	2.8	ND	2.2	59
SCN ⁻	<4	70		10.9	17.1	110	137	79	105
H ₂ S		<10		43.9	53.5	1.1	4.5	18	79
S ₂ O ₃ ²⁻				4.8	7.8	18.5	16.4		
SO ₃ ²⁻			12	<1	<1	<1	<1	10	12
SO ₄ ²⁻		1,000	55	56	49	461	541	225	65
PO ₄ ³⁻	0.06	60	0.1	2	3	0.1	2.8	3.7	0.6
Chloride	110	300	34	23	13	153	158	22	493
Methanol				ND	ND	<0.1	<0.1		
NO ₂ ⁻	<0.02		<0.5					1.4	0.9
NO ₃ ⁻			<0.01						
Fluoride	0.71	200	2					1.8	25
Total Sulfur	18								30
NH ₃ fixed	<30								
Carbonate	2x10 ⁶								

^aUnits are mg/L unless otherwise noted.

^bPurified sewage used as process feedwater.

^cCooling tower makeup water used as process feedwater.

^dBlanks mean parameter not analyzed.

^eND = not detected.

TABLE 4. CONVENTIONAL POLLUTANTS IN LURGI COAL GASIFICATION WASTEWATERS^a

Gasification System Type of Wastewater	Lurgi at Sasolburg			Lurgi at Westfield		Lurgi-type at Koroza		
	Raw Gas Liquor	Extracted Gas Liquor	Stripped Coal Liquor Slurry Water	Gas Liquor	Gas Liquor	Cyanic Water	Gas Liquor	Quenched Ash Water
pH, standard units	9.0	10.4	6.5	7.63	8.1	11.9	9.2	8.1
TDS	1,180 ^e	390 ^e	420 ^e	1,140	1,940	590	2,170	2,100
TSS	<1	<1	<1	f		140	150	8,760
Conductivity (umho/cm)	3,100	330	140					
COD	12,000	990	1,400	5,900	18,600	205	18,900	1,460
TOC							4,970	
BOD				4,300	12,250		9,030	90
NH ₃ (Total)	6,600	5,500	390	25				
CN ⁻		0.85	0.17	16	8		<1	0.01
SCN ⁻				210	60		<75	0.026
H ₂ S	720	170	8	220	330			Trace
SO ₃ ²⁻	240	55	40					Trace
SO ₄ ²⁻	8.7	5.2	16.0					495
PO ₄ ³⁻								
Chloride	1,690	950	600	160	9			28
NO ₃ ⁻	99	12	<1				<1	4.8
NO ₂ ⁻	0.15	0.03	0.04				Trace	0.4
Fluoride	45	40	50					0.91
Calcium	3.2	1.9	2.9					
Magnesium	0.51	0.46	1.0					
Sodium	6.0	6.5	6.1					
TDS after ignition				20	30			
Total Sulfur				340	450	60	84	
Fatty acids as acetic				260	1,050			
NH ₃ free				4,090	8,930		3,510	Trace
fixed				250	470		250	1.9
Carbonate				10,650	19,960			
Total solids						730	2,230	10,900
Total non-volatile solids						560		
Permanganate Number						570	14,200	8,060
Tar & oils							<400	

^aUnits are mg/L unless otherwise noted.

^bWastewater associated with Pittsburgh No. 8 coal.

^cWastewater associated with Montana Rosebud coal.

^dIncludes coal bunker vent gas scrubber and ash lock vent gas scrubber blowdowns.

^eTDS measured at 180°C.

^fBlanks mean parameter not analyzed.

^gPossible analytical interferences.

Of lower contaminant strength than the gas liquors are the condensates from gas cooling and acid gas removal (Rectisol). These waters also contain pollutants and are regarded as major wastewater sources. Ash pan water contains little organic contamination, but is a high dissolved solids stream. Streams that are not adequately characterized by the available data are the cyclone dust quench waters from the Wellman-Galusha process and the quenched ash water from the Lurgi process. Initial data indicate that they may present a significant source of aqueous phase pollution.

Trace Elements--

The trace elements present in fixed-bed gasification wastewaters are presented in Table 5 for the Foster-Wheeler/STOIC, Lurgi, Riley, Chapman, and Wellman-Galusha gasifiers. These data indicate that significant trace element concentrations are found in ash and coal handling aqueous waste streams. Specifically, these streams are ash pan water, cyclone dust quench water, and coal slurry water. Quench condensates present the next major level of trace element concentrations while acid gas removal condensates have slightly lower levels for most of these pollutants. The cyanic water from the Lurgi-type (Kosovo) facility did contain significant concentrations of sulfur, sodium, potassium, magnesium, iron, and chlorine. This is probably a coal dependent phenomenon, although high concentrations of sulfur are expected in Rectisol blowdowns because the process is designed to remove hydrogen sulfide and other sulfur compounds.

Lurgi process gas liquors contain high concentrations of arsenic, calcium, chromium, iron, magnesium, mercury, phosphorus, potassium, selenium, silicon, and sodium. The Chapman quench condensates contained many of the same trace elements as the Lurgi gasifier in addition to elevated levels of boron and fluorine.

Barium, calcium, chlorine, iron, potassium, strontium, and sulfur seem to be the major components in ash pan water. The cyclone dust quench water from the Wellman-Galusha gasifier contained elevated concentrations of aluminum,

TABLE 5. TRACE ELEMENTS IN FIXED-BED COAL GASIFICATION WASTEWATERS^a

Gasification System	Poster-Wheeler/STOIC	Lurgi at Sasolburg		Lurgi-type at Kosofo		Riley	Chapman at Fort Snelling	Wellman-Galusha
Type of Wastewater Method of Analysis	Ash Pan SSMS ^b	Raw Gas Liquor ICPE ^c	Extracted Gas Liquor ICPE ^c	Stripped Coal Slurry Water ICPE ^c	Cyanic Water SSMS	Phenol Effluent SSMS	Separator Liquor SSMS	Cyclone Dust Quench Water SSMS
Aluminum	30	<50	<50	<50	70	100	ND	MC ^{f,g}
Antimony	ND ^h	<2	85	36	ND	ND	70	<60 ⁱ
Arsenic	30	1,800 ⁱ	1,700 ⁱ	1,700 ⁱ	90	20	800	120 ⁱ
Barium	4,000	200	80	110	20	50	300	570 ^g
Beryllium	ND	<0.5	<0.5	<0.5	ND	ND	ND	ND
Boron	400	32	26	28	20	100	9,000	990 ^g
Bromine	100	ND	<2	<2	100	9	ND	40
Cadmium	ND	<2	<2	51	ND	ND	5	<5 ^g
Calcium	MC	3,200	1,900	MC	ND	6,000	2,000	MC ^g
Cerium	ND	ND	ND	ND	ND	ND	3	2
Cesium	<1	ND	ND	ND	4	ND	1	4
Chlorine	700	ND	ND	ND	4,000	1,000	200	MC
Chromium	40	1,500	2,800	3,900	9	5	ND	<5 ^g
Cobalt	5	<6	<6	<6	53	3	ND	9
Copper	20	<1	15	19	20	30	10	12 ^g
Fluorine	50	ND	ND	ND	300	4,000	2,000	2,000
Gallium	20	ND	ND	ND	ND	ND	ND	20
Germanium	ND	ND	ND	ND	20	30	ND	7
Iodine	7	ND	ND	ND	400	20	300	6
Iron	9,000	430	520	5,600	4,000	500	1,000	4,900 ^g
Lanthanum	ND	ND	ND	ND	8	ND	1	ND
Lead	10	<2 ⁱ	<2 ⁱ	61 ⁱ	8	70	ND	95 ^g
Lithium	200	<1	18	28	2	3	3	40
Magnesium	300	510	460	1,000	MC	2,000	2,000	MC
Manganese	<1	<1	<1	<1	40	10	ND	<1 ^g
Mercury	4.2 ⁱ	660 ⁱ	79 ⁱ	6.2 ⁱ	ND	ND	<0.0003	0.4 ⁱ
Molybdenum	20	<2	<2	<2	ND	ND	ND	4
Nickel	2	<3	4	3	7	80	ND	<20 ^g

(continued)

TABLE 5. (continued)

Gasification System	Foster-Wheeler/ STOIC		Lurgi at Sasolburg			Lurgi-type at Kosovo		Riley		Chapman at Fort Snelling	
	Ash Pan	Raw Gas Liquor	Extracted Gas Liquor	Stripped Gas Liquor	Coal Slurry Water	Cyanic Water	Phenolvan Effluent	Ash Pan	Separator Liquor	Cyclone Dust Quench Water	SSMS
Type of Wastewater Method of Analysis	SSMS ^b	ICPES ^c	ICPES	ICPES	ICPES	SSMS	SSMS	AAS ^d	SSMS	SSMS	SSMS
Micobium	2					ND	ND		8	ND	ND
Phosphorus	100	<200	<200	<200	3,200	ND	80		MC	400	MC
Potassium	6,000	<40	<40	2,400	<40	7,000	1,000		MC	MC	20
Rubidium	30					<1	55		ND	ND	ND
Scandium	<2	600 ⁱ	300 ⁱ	89 ⁱ	9 ⁱ	52	30	<7	2	2,000	6
Selenium	400	7,900	7,700	7,800	MC	1,000	1,000		2,000	2,000	2,000
Silicon	ND	<2	<2	<2	<2	ND	ND	14	2	2	2
Silver	200	6,000	6,500	6,100	MC	>4,000	4,000		ND	MC ^g	MC ^g
Sodium	MC	14	3	15	1,900	10	20		ND	1,100 ^g	1,100 ^g
Strontium	>9,000				MC	MC	MC		ND	MC ^g	MC ^g
Sulfur	4	<2 ⁱ	<2 ⁱ	<2 ⁱ	<2 ⁱ	ND	ND		ND	ND	ND
Tellurium	ND					ND	ND		ND	ND	ND
Thallium	<10					40	10		ND	ND	ND
Thorium	ND					ND	20		30	180 ^g	180 ^g
Tin	200	<5	<5	12 ⁱ	1,800	ND	400	20		100	100
Titanium	<10					≤10	≤30		10	ND	ND
Uranium	1	<3	<3	13 ⁱ	810	ND	1	3	ND	ND	ND
Vanadium	ND					ND	ND		5	2	2
Ytterbium	50	<2	<2	<2	190	30	≤30		ND	ND	ND
Yttrium	40	8	11	29	<3	50	70	5.3	ND	35 ^g	35 ^g
Zinc	10					ND	≤30		10	5	5
Zirconium											

^aUnits are ug/L unless otherwise noted.^bSSMS - spark source mass spectrometry.^cICPES - induced coupled argon plasma emission spectrometry.^dAAS - atomic absorption spectrophotometry.^ePlants mean parameter not analyzed.^fMC - major component in the wastewater, concentration greater than 10,000 ug/L.^gAnalyzed by induced coupled argon plasma emission spectrometry.^hNot detected.ⁱAnalyzed by atomic absorption spectrophotometry.

calcium, chlorine, fluorine, iron, magnesium, silicon, sodium, strontium, and sulfur.

The trace elements present in non-tar producing gasification wastewaters are presented in Table 6 for the Koppers-Totzek, Texaco, and KRW-PDU gasifiers. Although data are not available for the trace element content in gas quench condensates from the Koppers-Totzek process, data sources for the Texaco gasifier indicate that entrained flow gasifier quench condensates will contain elevated concentrations of a great number of elements. Major trace elements found in Texaco gas liquors are aluminum, barium, boron, calcium, chromium, fluorine, gallium, germanium, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, phosphorus, rubidium, selenium, silicon, sodium, strontium, sulfur, titanium, zinc, and zirconium. Calcium is the only major trace element in slag water from the Texaco process.

Gas compression and cooling condensates from the Koppers-Totzek process contain elevated concentrations of calcium, fluorine, iron, magnesium, potassium, selenium, sodium, sulfur, and zinc. Trace elements found in acid gas removal wastewaters from this entrained-bed process included elevated concentrations of calcium, iron, magnesium, potassium, silicon, sodium, sulfur, and zinc.

The level of dissolved elements in the wastewater blowdown from the KRW-PDU is presented in Table 6. Soluble elements such as boron, barium, calcium, iron, potassium, magnesium, and sodium were detected in the blowdown with each test coal. Although arsenic and selenium were detected in the KRW-PDU wastewater for each of the tests, other elements with similar volatility (i.e., beryllium, cadmium, lead, molybdenum, antimony, and thallium) were not observed.

The boron, potassium, and sodium levels associated with the lignite test were an order of magnitude higher than levels for the sub-bituminous or bituminous tests. This is consistent with their concentrations in the lignite

TABLE 6. TRACE ELEMENTS IN NON-TAR PRODUCING COAL GASIFICATION WASTEWATERS^a

Gasification System	Koppers-Totzek at Modderfontein				KRW-FPU		Buhrtoble/Ruhrchemie		Texaco at	
Type of Wastewater Method of Analysis	Compressor Condensate ^b SSMS	Compressor Condensate ^c SSMS	Rectinol ^b SSMS	Rectinol ^c SSMS	Sub-bituminous AAS ^d /ICPES	Bituminous AAS/ICPES	Lignite AAS/ICPES	Settler Underflow SSMS	Settler Underflow AAS/ICPES	
Aluminum	5	9	100	100	ND ^g	1,400	2,400	MC ^h	MC	
Antimony	<2	10	<1	<1	ND	ND	ND	90	21	
Arsenic	2	4	20	10	73	300	420	600	480	
Barium	100	40	200	200	1,200	550	470	MC	2,700	
Beryllium	ND	ND	ND	ND	ND	ND	5	10	130	
Bismuth	2	ND	ND	ND	1	10,000	MC	10	MC	
Boron	<1	<1	<1	ND	6,800	ND	ND	700	MC	
Bromine	80	300	30	60	ND	ND	ND	300	190	
Cadmium	3	7	1	MC	ND	MC	8,000	70	MC	
Calcium	MC	MC	1	ND	MC	ND	ND	1,000	MC	
Cerium	ND	1	<1	ND	ND	ND	ND	70	MC	
Cesium	<1	ND	200	300	ND	ND	ND	4,000	1,200	
Chlorine	100	60	3	7	ND	ND	12	400	260	
Chromium	5	5	1	<1	ND	5	ND	700	740	
Cobalt	3	1	1	100	ND	ND	ND	50	MC	
Copper	10	10	50	ND	ND	ND	ND	20	MC	
Dysprosium	ND	ND	ND	ND	ND	ND	ND	20	MC	
Erbium	ND	ND	ND	ND	ND	ND	ND	10	MC	
Europium	ND	ND	ND	ND	ND	ND	ND	MC	MC	
Fluorine	30	3,000	400	3,000	ND	ND	ND	30	30	
Gadolinium	ND	ND	ND	<1	ND	ND	ND	2,000	2,000	
Gallium	<1	3	<1	<1	ND	ND	ND	3,000	3,000	
Germanium	5	7	<1	2	ND	ND	ND	20	20	
Hafnium	ND	ND	ND	ND	ND	ND	ND	30	30	
Holmium	ND	ND	ND	ND	ND	ND	ND	20	20	
Iodine	4	8	8	9	1,800	600	2,300	MC	MC	
Iron	500	1,000	MC	2,000	ND	ND	ND	900	900	
Lanthanum	ND	1	1	ND	ND	ND	ND	MC	MC	
Lead	ND	30	20	10	ND	ND	ND	4,000	3,100	
Lithium	20	10	6	3	ND	100	44	70	2	
Luettium	3	ND	ND	ND	ND	ND	55,000	MC	MC	
Magnesium	1,000	2,000	MC	MC	28,000	7,600	ND	MC	2,500	
Manganese	10	9	50	80	ND	610	ND	MC	MC	

(continued)

TABLE 6. (continued)

Gasification System	Koppers-Totzek at Modderfontein				KRM-FDU		Texaco at Ruhrkohle/Ruhrchemie		
	Compressor, Condensate SSMS	Compressor, Condensate ^c SSMS	Rectisol ^b SSMS	Rectisol ^c SSMS	Sub-bituminous AAS/ICPES	Bituminous AAS/ICPES	Lignite AAS/ICPES	Settler Underflow SSMS	Settler Underflow AAS/ICPES
Type of Wastewater Method of Analysis									
Molybdenum	30	20	40	20	ND	ND	ND	1,000	1,100
Niodymium	ND	ND	ND	ND	ND	ND	ND	100	100
Nickel	4	7	200	100	ND	ND	ND	1,000	1,050
Niobium	2	5	2	<1	ND	ND	ND	200	200
Phosphorus	70	70	700	1,000	1,300	ND	ND	MC	MC
Potassium	MC	MC	5,000	MC	2,700	4,300	MC	MC	5,800
Praseodymium	ND	ND	ND	ND	ND	ND	ND	100	MC
Rubidium	8	3	9	6	ND	ND	ND	2,000	100
Samarium	ND	ND	ND	ND	ND	ND	ND	90	90
Scandium	<1	<1	<1	<1	38	ND	ND	1,000	1,600
Selenium	1,000	2	50	40	MC	ND	ND	MC	MC
Silicon	300	100	1,000	2,000	ND	ND	ND	MC	MC
Silver	52	1	ND	ND	MC	ND	ND	<6	MC
Sodium	2,000	<1,000	>1,000	>2,000	MC	8,600	MC	7,000	MC
Strontium	70	30	300	500	ND	ND	ND	MC	MC
Sulfur	>2,000	>3,000	>2,000	>4,000	ND	ND	ND	MC	MC
Tantalum	2	ND	ND	ND	ND	ND	ND	5	5
Tellurium	3	3	ND	ND	ND	ND	ND	7	7
Terbium	ND	ND	ND	ND	ND	ND	ND	1	1
Thallium	ND	ND	ND	ND	ND	ND	ND	100	100
Thallium	ND	ND	ND	ND	ND	ND	ND	200	200
Thorium	<8	<3	<3	<6	ND	ND	ND	4	4
Thulium	ND	ND	ND	ND	ND	ND	ND	100	100
Tin	2	<1	4	ND	ND	ND	ND	MC	MC
Titanium	30	200	100	200	46	18	110	MC	MC
Tungsten	ND	ND	ND	ND	ND	ND	ND	50	50
Uranium	<7	<3	6	6	20	14	ND	300	300
Vanadium	2	<1	3	5	ND	ND	ND	2	2
Vanadium	ND	ND	ND	ND	ND	ND	ND	20	20
Ytterbium	ND	ND	<1	<1	ND	ND	ND	700	700
Yttrium	<1	1	6,000	5,000	ND	ND	ND	MC	MC
Zinc	600	1,000	ND	ND	ND	ND	ND	1,000	1,700
Zirconium	3	10	<1	<1	ND	ND	ND	MC	MC

^aUnits as ug/L unless otherwise noted.^bPurified sewage used as process feedwater.^cCooling tower makeup water used as process feedwater.^dSSMS - spark source mass spectrometry.^eAAS - atomic absorption spectrophotometry.^fICPES - induced coupled argon plasma emission spectrometry.^gND - not detected.^hMC - major component in the wastewater, concentration greater than 10,000 ug/L.ⁱBlanks mean parameter not analyzed.

feedstock which were also higher than in the other coals. In addition the KRW-PDU was operated with less fresh water makeup and, therefore, less wastewater blowdown during the lignite test.

Organics--

Wastewaters were analyzed to determine the concentrations of organic species judged to be of environmental concern. These compounds were primarily priority pollutants in the Base/Neutral and Acid extractable groups and the Appendix C extractable compounds. These organics were deemed important because of their regulatory significance. Volatile (purgeable) organic compounds included halogenated organics and aromatics; however, selected halogenated compounds, priority pollutant pesticides, and PCBs were excluded from the analysis because of their low probability of occurrence in coal gasification wastewaters. Organics analysis for fixed-bed gasifier wastewaters included an additional set of known or suspected carcinogenic compounds that were selected because of the probability that they will be present in the wastewaters. The actual listing of compounds is presented in the various source test and evaluation documents (3,6,8,9). The procedures used for the extraction and analysis of wastewater samples are also presented in these documents (14,15). In general, a given compound was assumed to be not detected in a wastewater if it was not found at a concentration less than the lowest detection limit for the various extractable groups in that wastewater.

The organics found in fixed-bed gasifier wastewaters are presented in Table 7 for the Chapman, Foster-Wheeler/STOIC, Riley, and Lurgi-type gasifiers. These data indicate that the majority of the extractable organics are present in quench condensates and that ash pan water is relatively low in these compounds. Analysis of Chapman separator liquor indicated that of the identified compounds, the phenolics account for about 99 percent of the total chromatographable organics. Methylphenols contribute the majority of the phenolics identified, with phenol the next largest contributor. Of the base/neutrals, the compounds present in the greatest concentrations are the

TABLE 7. ORGANICS IN FIXED-BED COAL GASIFICATION WASTEWATERS^a

Gasification System	Chapman		Foster Wheeler/ STOIC	Riley	Lurgi-type at Kosovo
	Separator Liquor		Ash Pan Water	Ash Pan Water	Phenoxolvan Inlet Water
Wastewater Type					
Sample Type	Average ^b	Range	grab	grab	grab
Acid Extractable Compounds					
Phenol	2,400	1900-3400	0.0033	241	690
Methylphenols	3,200 ^c	1500-4700	ND	ND	— ^e
Dimethylphenols (total) ^f	1,200	330-1900	ND	ND	333
2,4-Dimethylphenol	420 ^g	98-820	ND	ND	130
Trimethylphenol	0.82	0.35-2.2	ND	ND	ND
Indanol	1.7	<0.07-3.2	ND	ND	ND
1-Naphthol	5.0	3.3-8.5	ND	ND	ND
2-Naphthol	6.7	5.4-9.2	ND	ND	ND
Resorcinol/Catechol	30	3.6-65	ND	ND	ND
Hydroxybenzaldehyde	5.7	<0.18-19	ND	ND	ND
o-Cresol	—	—	ND	ND	260
m-Cresol	—	—	ND	ND	610
p-Cresol	—	—	—	—	100
Total Unknown Phenols	—	—	—	—	698
Base-Neutral Extractable Compounds					
Naphthalene	8.6	1.6-17	0.00033	7.4	ND
Acenaphthalene	3.6	1.2-6	ND	2.0	ND
Fluorene	2.6	0.28-6	ND	1.0	ND
Phenanthrene/Anthracene	2.3	0.7-6	ND	2.2	ND
Fluoranthene	5.7	0.3-9	ND	1.7	ND
Pyrene	5.7	0.4-9	ND	1.7	ND
Bis(2-ethylhexyl)phthalate	12	1.2-32	0.0067 ^h	11.1	ND
Chrysene	0.12	—	ND	2.4	ND
Benzo(b)fluoranthene	0.10	—	ND	ND	ND
Benzo(a)pyrene	0.12	—	ND	ND	0.19
Pyridine	1.2	—	ND	ND	28
Ethylpyridine(s)	18	1.3-61	ND	ND	46
Quinoline	3.1	0.62-5.6	ND	ND	5
4-Methylquinoline	0.11	—	ND	ND	ND
1-Methylnaphthalene	2.3	0.43-4.2	ND	ND	ND
2,3-Dimethylnaphthalene	2.3	0.65-4.5	ND	ND	ND
2,6-Dimethylnaphthalene	2.2	<1.3-3	ND	ND	ND
Indole	12	8-14	ND	ND	ND
2-Methylindole	12	2.2-16	ND	ND	ND
3-Methylindole	2.4	0.58-3.6	ND	ND	ND
Diethyl phthalate	ND	—	ND	1.9	ND
Di-n-butyl phthalate	ND	—	ND	1.4	ND
2-Methylpyridine	—	—	—	—	29
3- and 4-Methylpyridine(s)	—	—	—	—	13
Alkylpyridine(s)	—	—	—	—	26
Alkylquinoline(s)	—	—	—	—	12
Benzo(a)anthracene	—	—	—	—	0.92
7,12-Dimethylbenzo(a)anthracene	—	—	—	—	0.23
Benzo(b)fluoranthene	—	—	—	—	0.68
3-Methylcholanthrene	—	—	—	—	<0.004
Dibenz(a,h)anthracene	—	—	—	—	0.02
252 Group (as Benzo(a)pyrene)	—	—	—	—	1.26
Volatile Organic Compounds					
Benzene	0.63	0.56-0.74	—	—	0.9
Toluene	0.42	0.38-0.46	—	—	0.5
Ethylbenzene	0.048	0.022-0.106	—	—	ND
m,p-Xylene	0.15	0.124-0.172	—	—	ND
o-Xylene	0.28	0.034-0.184	—	—	0.8

^a All data as mg/L.^b Average of grab samples.^c One data point not included in the average was rejected due to extremely high value, but compound was identified 6 of 6 times.^d ND means not detected.^e Dashes mean parameter not analyzed.^f Includes 2,4-DMP.^g The portion of 2,4-DMP from the B/N fraction was estimated from the amount found in the acid fraction.^h Probable artifact of sample handling.

indoles and the naphthalenes. The volatile organic compounds were identified at concentrations generally 2 to 4 orders of magnitude lower than the extractable compounds. Analysis of Lurgi-type gas liquors identified many of the same pollutants, albeit at lower concentrations. However, a different group of polynuclear aromatics characterized this wastewater. These organic data are consistent with observations made by others (16,17,18).

The Riley gasifier ash pan water contained phenol and a variety of polynuclear aromatics. No major organic contamination was found in ash pan water from the Foster-Wheeler/STOIC gasifier, however.

The organics found in non-tar producing gasifier wastewaters are presented in Table 8 for the Koppers-Totzek, Texaco, and KRW-PDU gasifiers. As is characteristic of entrained-bed gasifiers, process wastewaters contain little or no organic contamination. However, low levels of polynuclear aromatics were found in acid gas removal blowdowns from the Koppers-Totzek process. The results of organic analysis of the KRW-PDU wastewater blowdown are presented in Table 8. Values are for total (dissolved and suspended) organics since the samples collected from the wastewater separator pit contained suspended solids (0.1 to 0.5 percent). The organic extraction procedure used prior to analysis was performed on water plus solids. Naphthalene was the major organic compound present in the wastewater. Additional multi-ring organic compounds of higher molecular weight were also detected in these waters. All compounds detected in the wastewaters with molecular weight less than 202 were also observed in the raw product gas (12). The dissolved organic levels of naphthalene, fluorene, phenanthrene, fluoranthene, pyrene, and pyridine were significantly lower than the total after suspended solids separation (12).

Ash Sluice Water

Conventional Pollutants--

Conventional pollutants in ash sluice waters from the Wellman-Galusha gasifier are presented in Table 9. These data are grouped with wastewater

TABLE 8. ORGANICS IN NON-TAR PRODUCING COAL GASIFICATION WASTEWATERS^a

Gasification System	Koppers-Totzek at Modderfontein		KRW-PDU			Texaco- Ruhrkohle/ Ruhrchemie
Wastewater Type	Compressor Condensate grab	Rectisol grab	Sub-bituminous	Bituminous	Lignite	Settler Underflow grab
Sample Type						
<u>Acid Extractable Compounds</u>						
Phenol	Tr ^b	Tr	0.19 ^c	--	0.16	0.0026
Dimethylphenols (total) ^d	ND ^e	ND	--	--	--	ND
2,4-Dimethylphenol	ND	ND	--	--	--	ND
o-Cresol	ND	ND	ND	--	ND	ND
m-Cresol	ND	ND	ND	--	ND	ND
p-Cresol	--	--	ND	--	ND	--
Total Unknown Phenols	--	--	--	--	--	--
<u>Base-Neutral Extractable Compounds</u>						
Naphthalene	Tr	Tr	10.0	0.26	0.20	ND
Acenaphthalene	ND	Tr	1.0	0.040	0.060	ND
Fluorene	ND	0.001	1.0	0.10	0.11	ND
Phenanthrene/Anthracene	ND	Tr-0.0046	2.71	0.44	0.040	ND
Fluoranthene	ND	0.0063-0.019	0.94	0.30	0.001	ND
Pyrene	ND	0.025-0.097	0.68	0.36	0.001	ND
Bis(2-ethylhexyl)phthalate	Tr ^f	ND	--	--	--	0.0081 ^f
Chrysene	ND	0.034	ND	0.020	ND	ND
Benzo(b)fluoranthene	ND	0.002	ND	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND	0.005	ND	ND
Pyridine	ND	ND	ND	Tr	0.25	--
Diethyl phthalate	Tr ^f	Tr ^f	--	--	--	ND
Di-n-butyl phthalate	0.006 ^f	ND	--	--	--	ND
Benzo(a)anthracene	ND	0.016-0.023	ND	0.010	ND	ND
Benzo(b)fluoranthene	ND	0.015	--	--	--	ND
Dibenz(a,h)anthracene	ND	ND	--	--	--	ND
<u>Volatile Organic Compounds</u>						
Benzene	ND	ND	0.15-1.10	0.007	0.020	--
Toluene	ND	ND	--	--	--	--
Ethylbenzene	ND	ND	--	--	--	--
m,p-Xylene	ND	ND	--	--	--	--
o-Xylene	ND	ND	--	--	--	--
Chloroform	Tr	Tr	--	--	--	--
Total Volatile Organics	--	--	--	--	--	0.03-0.05

^aAll data as mg/L.^bTr means trace (detected but at an unquantifiable level below 0.001 mg/L).^cDashes mean parameter not analyzed.^dIncludes 2,4-DMP.^eND means not detected.^fProbable artifact of sample handling.

TABLE 9. CONVENTIONAL POLLUTANTS IN ASH SLUICE WATER FROM FIXED-BED GASIFICATION FACILITIES

Parameter	Lurgi-type at Kosovo ^a		Wellman-Galusha at Glen Cery		Wellman-Galusha at Fort Snelling	
	Grab ^b	Range of Grabs	Grab	Grab	Grab	Grab
Water Quality Parameters						
pH	8.1	8.1-12.1	NA ^c		9.3	
Total Solids (mg/L)	10,900	1300-11500	NA		NA	
Total Non-Volatile Solids (mg/L)	5,700	130-5700	NA		NA	
Total Suspended Solids (mg/L)	8,760	570-8760	550		NA	
Total Dissolved Solids (mg/L)	2,100	760-2600	400		4,300	
COD (as mgO ₂ /L)	1,460	d	NA		76	
Permanganate (as mgO ₂ /L)	8,060		NA		NA	
BOD ₅ (as mgO ₂ /L)	90	30-90	40		64	
Composition Data (mg/L)						
TOC	NA		140		16	
Tars and Oils	MF ^e		MF		MF	
Phenols	0.17	0.04-0.3	NA		0.36	
Free Ammonia	Tr ^f		NA		NA	
Fixed Ammonia	1.9	1.5-2.5	<3		5.4	
Cyanide	0.01	Tr-0.01	0.06		<0.02	
Nitrites	0.40	0.05-0.82	NA		<0.01	
Nitrates	4.8	4.0-5.6	17		3	
Chlorides	28.0	20-37	17		78	
Fluorides	0.91	0.65-1.2	0.6		0.87	
Sulfites	Tr		NA		47	
Sulfates	495	320-670	95		2,860	
Sulfide	Tr		3		NA	
Thiocyanate	0.026	0.01-0.04	2		NA	
Thiosulfates	Tr		NA		NA	

^aQuenched ash water.^bMost representative grab sample.^cNot available.^dBlanks mean single grab collected.^eNot found.^fTrace.

characterization information for Lurgi-type quenched ash water. This stream can be characterized as either an ash sluice water or an ash pan water. However, the oxygen demand contamination levels in Lurgi-type quenched ash water are much higher than either of the Wellman-Galusha ash quenching streams. The similarities between these streams can be identified from the concentrations of BOD, phenols, ammonia, cyanide, nitrite, nitrate, chloride, and fluoride in the wastewaters. However, differences in the level of dissolved solids, chemical oxygen demand, and sulfur species in each wastewater are apparent. This probably is a coal-dependent phenomenon.

Trace Elements--

The trace elements present in both the Glen-Gery and Fort Snelling Wellman-Galusha gasifier ash sluice waters are presented in Table 10. These data indicate the presence of elevated concentrations of aluminum, boron, calcium, chlorine, iron, magnesium, silicon, sodium, strontium, sulfur, tin, and titanium in the ash sluice waters from fixed-bed gasifiers. Significant differences in the concentrations of aluminum, boron, calcium, chlorine, sodium, and sulfur in ash sluice waters are apparent between the two Wellman-Galusha gasifiers. Apparently, this is a coal dependent phenomenon.

Solids Leachates

Conventional Pollutants--

Samples of ash, cyclone dust, and fine and coarse slag were subjected to the ASTM leaching test to define the solubility of components in these solid wastes. The ASTM test exposes the solid to deionized water at a 1:4 (solid: water) ratio for 48 hours to simulate leaching of compounds from a solid. The results of water quality analyses of ASTM leachates from gasification slag and ash are presented in Table 11 for the Lurgi, Wellman-Galusha, and Texaco gasifiers. On the basis of available conventional pollutant data for the slag and ash leachates from the different gasification processes, the fixed-bed gasifier leachates are generally higher in dissolved solids and chemical oxygen demand than leachates from entrained-bed gasifiers. The wastewaters

TABLE 10. TRACE ELEMENTS IN ASH SLUICE WATER FROM FIXED-BED GASIFICATION FACILITIES^a

Method of Analysis	Wellman-Galusha at Glen Gery	Wellman-Galusha at Fort Snelling
	SSMS ^b	ICPES ^c
Aluminum	d	MC ^e
Antimony		2 ^f
Arsenic		3.3
Barium		130
Beryllium	1	
Boron	1	4,600
Bromine	10	20 ^g
Cadmium	3	<2 ^g
Calcium	10,000	MC
Cerium	100	2 ^g
Cesium	3	
Chlorine	MC	MC
Chromium	500	7
Cobalt	40	<2 ^g
Copper	100	17
Dysprosium	3	
Erbium	1	
Europium	1	
Fluorine	600	870
Gadolinium	2	
Gallium	40	8 ^g
Germanium	1	
Holmium	2	
Iodine	1	
Iron	5,000	1,200
Lanthanum	50	<1 ^g
Lead	20	8 ^g
Lithium	400	400 ^g
Lutetium	1	
Magnesium	5,000	MC
Manganese	10	2
Mercury		1.4 ^f
Molybdenum	400	310
Neodymium	10	
Nickel	30	20
Niobium	30	2 ^g
Phosphorus		400 ^g
Potassium	6,000	MC
Praseodymium	10	1 ^g
Rubidium	200	40 ^g
Samarium	10	
Scandium	7	
Selenium	20	20 ^f
Silicon	10,000	300 ^g
Silver	2	1 ^g
Sodium	1,000	MC
Strontium	3,000	4,000
Sulfur		MC
Terbium	1	
Thorium	40	
Thulium	1	
Tin	4	3,000
Titanium	10,000	44
Tungsten	10	20 ^g
Uranium	10	
Vanadium	500	77
Ytterbium	2	
Yttrium	40	
Zinc	70	44
Zirconium	200	2

^aUnits as ug/L unless otherwise noted.

^bSSMS - spark source mass spectrometry.

^cICPES - inductively coupled argon plasma emission spectrometry.

^dBlanks mean parameter not analyzed.

^eMC - major component, concentration >10,000 ug/L.

^fAnalyzed by atomic absorption spectrophotometry.

^gAnalyzed by spark source mass spectrometry.

TABLE 11. CONVENTIONAL POLLUTANTS IN ASTM LEACHATES FROM GASIFICATION SLAG AND ASH^a

Gasification System	Lurgi at Sasolburg		Wellman-Galusha at Glen Gery		Wellman-Galusha at Fort Snelling		Texaco at Ruhrkohle/Hutchinson	
	Ash		Ash	Cyclone Dust	Ash	Cyclone Dust	Settler Fines	Coarse Slag
Initial pH, standard units	5.0	b			4.13	4.04	8.5	7.0
Final pH, standard units	8.4						810	
Alkalinity as CaCO ₃	14							
Bicarbonate	14							
Carbonate	<1				<1	<1	80	
TOC	<1							
COD	44			1,800	1,710	1,410		
BOD					2,970	3,150		
Chloride	16	5.7		6.7			120	
Fluoride	0.2			4.4			8.7	
TDS	1,820			2,040	2,130	2,280	18	420
TSS				40	36	17		
Conductivity (umho/cm)	1,530						1,580	660
CN ⁻					<0.02	0.05	0.09	
SCN ⁻							18	
Sulfide	<1							
Sulfite	8				<10	<10		
NO ₃ ⁻ as N	0.3				<0.25	<0.25	ND ^c	
NO ₂ ⁻ as N		0.05		0.5	<0.01	<0.01	ND	
PO ₄ ³⁻ as P		0.03			0.1	0.2	ND	
NH ₄ ⁺ as N		0.5		<0.05	<0.007	1.8	210	
Ca ²⁺		4		10.0				
Mg ²⁺		0.89		7.0				
Na ⁺		1.0		4.0				
Sulfate		2.2					<5	
Elemental sulfur	1,030	0.300		1.0				
Phenol					0.002	0.38	ND	

^aUnits are mg/L unless otherwise noted.

^bBlanks mean parameter not analysed.

^cNot detected.

are similar in their chemistries for most of the other pollutants, except for the ammonia level in leachates from Texaco settler fines. The ammonia present in Texaco fine slag leachates is several orders of magnitude higher than either of the fixed-bed gasifier ash leachates.

Trace Elements--

Samples of Chapman and Wellman-Galusha ash and cyclone dust, Lurgi ash and spent filter media, and Texaco fine and coarse slag were subjected to the RCRA leaching test to define the solubility of trace elements in these solids. The RCRA extraction procedure is a standard EPA procedure used to define the toxic/non-toxic nature of a solid waste. It utilizes a 1:20 (solid:liquid) ratio for extraction under acidic conditions. Acetic acid is added to the liquid to adjust the pH to 5.0 which is the control point for the test.

The results of elemental analyses of the RCRA leachates from gasification slag and ash are presented in Table 12 for the Chapman, Lurgi, Wellman-Galusha, and Texaco gasifiers. These data indicate that fixed-bed gasifiers produce ash leachates that contain elevated concentrations of barium, calcium, fluorine, iron, magnesium, potassium, silicon, sodium, sulfur, and zinc. The leachates from the extraction of Wellman-Galusha cyclone dust contain high levels of aluminum, calcium, chlorine, fluorine, magnesium, manganese, potassium, silicon, sodium, strontium, sulfur, and zinc. However, the extraction of Lurgi spent filter media from tar and oil separation produced leachates that contained only high concentrations of calcium and magnesium. These data indicate that leachates from the extraction of fixed-bed gasifier ash are within the current RCRA limits (set at 100 times the National Interim Primary Drinking Water Standards for Ag, As, Ba, Cd, Cr, Hg, Pb, and Se).

Major elements found in leachates from Texaco gasifier fine and coarse slags are aluminum, boron, calcium, magnesium, phosphorus, potassium, silicon, sodium, and zinc. These data also indicate that none of the eight RCRA listed elements approach the RCRA limit. Moreover, silver, arsenic, mercury, and selenium were not detected in fine and coarse slag leachates. The gasifier

TABLE 12. TRACE ELEMENTS IN RCRA LEACHATES FROM GASIFICATION SLAG AND ASH^a

Gasification System	Chesapeake		Lurgi		Wellman-Galusha at Glen Cove		Wellman-Galusha at Fort Snelling		Tosco at Rubidelo/Abasco		KIP-100	
	Ash	Slag ^b	Ash	Slag ^c	Ash	Slag ^c	Ash	Slag ^c	Settler Fines	Coarse Slag	Sub-bituminous	Bituminous
Type of Leachate												
Method of Analysis												
Aluminum	SPC ^d	SPC	<50	<50	6	2,000	100	<1,000	HC ^f	130	60,000	8
Antimony	10	20 ^j	<5	<5	4	30	<60	8	MD	MD	MD	MD
Arsenic	2,000	300	130	530	100	700	1,000	33	100	33	2900	700
Barium									MD	MD	MD	MD
Beryllium	20	2	<9	<9	20	700	80	100	3,900	180	MD	MD
Boron	SPC	SPC			2		<20	4	MD	MD	MD	MD
Bromine					1	5	MD	MD	MD	MD	MD	MD
Calcium	28,000	58,000	99	99	99	MD	MD	MD	MD	MD	MD	MD
Cadmium	SI								MD	MD	MD	MD
Cerium	200	300			160	2	1	1	MD	MD	MD	MD
Chlorine	200	300			2	2	1	1	MD	MD	MD	MD
Chromium	CI	SI			1	4	4	4	MD	MD	MD	MD
Cobalt	SPC	3			1	300	7	1	6	12	45	71
Copper	30	20			8	90	100	6	41	13		
Fluorine	3,000	SPC			60	MD	3,000	4,000				
Gallium	4	30 ^j			1		1	2				
Germanium	2											
Gold												
Iodine	5,000	SPC	590	20	10	1,000	2,000	600	29		220	MD
Iron					2	8	8	10	24		MD	MD
Lead	10	SPC	<2 ^h	<2 ^h	30	700	40	MD			3	MD
Lithium					30	500	MD	MD			MD	MD
Magnesium	>9,860	400	4,300	1,700	36	7,000	MD	MD	1,700	1,200	200	MD
Mercury	100	90	270	300	5	MD	500	100	320	190	MD	MD
Molybdenum												
Nickel	SPC	200 ^j	<2	<2	20	70	<0.5 ^h	<0.3 ^h		6	MD	MD
									330		26	MD

(cont. inside)

TABLE 12. (continued)

Gasification System	Dumas		Lurgi		Wellman-Galusha at Glen Gery		Wellman-Galusha at Fort Snelling		Tosco at McIntosh/Anschutze		FBI-PW	
Type of Lignite Method of Analysis	Ash	SPS ^b	Ash	SPS ^b	Ash	SPS ^b	Ash	SPS ^b	Settler Fines	Coarse Slag	Sub-bituminous	Bituminous
Phosphorus	SPC	SPC							1,400		NO	
Potassium	5,000	800		370	6,000	2	70	400	1,100	1,700		
Praseodymium												
Rubidium	3	SPC			2	2	20	20				
Selenium	<1	SPC		<1 ^b	<1	<1	14 ^b	6			NO	NO
Silicon	7,000	SPC		72	200	2,000	HC	HC	12,000	3,700	NO	NO
Silver		SPC		<1	5	2			800	1,800	NO	NO
Sodium	2,000	500		280	1,000	>4,000	2,000	3,000			2,600	
Strontium	3,000	100		660	60	6,000	6,000	7,000				
Sulfur	>9,700	400		350	300	HC	6,000	>6,000	48		NO	
Thallium						<1	<8	<10				
Thorium												
Tin	100	SPC		<5	1	2,000	100	50			NO	
Titanium					7	<10	<6	<10				
Uranium				<1	3	2	7	3		3	NO	
Vanadium						4	7	3				
Yttrium				18	4,000	HC	100	70	HC	88	480	
Zinc	SPC	SPC			30	4	30					
Zirconium												

^aUnits as ug/L unless otherwise noted.

^bSPS - Spark source mass spectrometry.

^cSPS - Inductively coupled argon plasma emission spectrometry.

^dAAS - Atomic absorption spectrophotometry.

^eSPC - Less than or equal to the concentration of the element in the blank.

^fHC - Major component in the wastewater, concentration >10,000 ug/L.

^gBlanks were present but not analyzed.

^hAnalyzed by atomic absorption spectrophotometry.

ⁱNO = not detected.

^jHeterogeneous electrode problem, actual concentration of element is likely to be less than stated value.

ash from the KRW-PDU was also subjected to RCRA leaching tests. None of the leachates of the ash approach the limits defined for the eight elements. The majority of the heavy metals were undetected or near the detection limit.

WASTEWATER BIOASSAY

An EPA Level 1 bioassay for health and ecological effects was performed during many of the source test and evaluation studies on quench condensates, ash sluice waters, treated discharges, and solid waste leachates. These tests were performed according to procedures detailed in the EPA Level 1 screening manual for environmental assessment (19). Level 1 is the screening phase of EPA's three-phase environmental assessment strategy and provides a general indication of the pollution potential of process and discharge streams.

The EPA Level 1 health effects bioassay is based on the following tests:

- *Salmonella* bacterial mutagenicity assay (AMES) and
- In vitro cytotoxicity assay: Chinese Hamster Ovary (CHO) clonal toxicity, Rabbit Alveolar Macrophage (RAM) toxicity, and human lung fibroblast cell (WI-38) toxicity.

The Ames assay is based on the ability of selected mutant strains of *Salmonella typhimurium* to revert from histidine dependence to the ability to synthesize nutriment from inorganic materials upon exposure to various mutagens and carcinogens. In vitro cytotoxicity assays employ mammalian or human cells in culture to measure quantitatively cellular metabolic impairment and/or death resulting from exposure, in vitro, to soluble or particulate toxic material.

The ecological effects bioassay is based on the following:

- *Selenastrum capricornutum* (fresh water alga) toxicity and

• Pimephales promelas (fathead minnow) toxicity.

These involve multiple assays for toxicity which are made by exposing a test organism (e.g., S. capricornutum or P. promelas) to the aqueous waste in order to determine the concentration of effluent estimated to cause a 50 percent decrease in the organism population over a finite time period.

Bioassay data for the various gasifier wastewaters and solid waste leachates are summarized in Table 13. These data indicate that only the raw Lurgi gas liquor produced a positive AMES test result; while treated quench condensates, cyclone dust quench waters, ash sluice waters, and solids leachates had negative AMES test results. These data also suggest that quench condensates from entrained-bed gasifiers are not mutagenic according to the AMES test.

In vitro cytotoxicity test results indicate that solids leachates from both fixed-bed and entrained-bed gasification processes have either low or no detectable toxicity. Leachates that show low cytotoxicity are produced from Riley ash and Texaco settler underflow fines. Lurgi raw and pretreated gas liquors show a moderate level of cytotoxicity while Texaco raw quench condensates produce a relatively high cytotoxic response in the CHO clonal assay. This is probably the result of particulate matter in these samples since the test measures acute cellular toxicity of particulates and associated chemical species. Of the other coal gasification aqueous waste streams, only Wellman-Galusha (Fort Snelling) ash sluice water produced a moderate cytotoxic response. This stream had a dissolved solids concentration that was an order of magnitude higher than the Glen-Gery Wellman-Galusha ash sluice water.

Ecological effects test data for the Chapman and Lurgi gasifier quench condensates indicate that treatment of aqueous wastes will reduce the toxic effects of these wastewaters on algae and fathead minnows. Apparently, biooxidation treatment effects the greatest degree of improvement toward the

TABLE 13. SUMMARY DATA FOR WASTEWATER BIOASSAY TESTS

Gasifier/Wastewater	AMES ^a	Bioassay Test Results ^c		
		In Vitro Cytotoxicity ^b	Freshwater Alga ^e EC ₅₀	Fathead Minnow ^d LC ₅₀
Lurgi-type Kosovo/gas liquor	positive	CHO-M	— ^g	—
Lurgi-type Kosovo/pretreated gas liquor	negative	CHO-M	—	—
Lurgi-type Kosovo/ASTM slag leachate	negative	CHO-MD	—	—
Lurgi Sasolburg/pretreated gas liquor	—	—	—	4.3 - 7.5%
Lurgi Sasolburg/bioreactor effluent	—	—	—	38%
Riley/ash leachate	negative	CHO-L	3% ^f	—
Riley/cyclone dust leachate	negative	CHO-MD	4%	—
Chapman/separator liquor	negative	RAM-MD	0.1 to 1.0%	0.02%
Wellman-Galusha (Fort Snelling)/ash sluice water	negative	WI-38-M	—	—
Wellman-Galusha (Fort Snelling)/cyclone dust quench water	negative	WI-38-MD	—	—
Wellman-Galusha (Glen-Gary)/ash sluice water	negative	WI-38-MD	—	—
Wellman-Galusha (Glen-Gary)/ash leachate	negative	WI-38-MD	—	—
Texaco Ruhrkohle/Ruhrchemie/settler underflow	negative	CHO-H	1.4 - 1.7%	1.2 - 1.3%
Texaco Ruhrkohle/Ruhrchemie/ASTM slag leachate	negative	CHO-MD	13 - 19%	—
Texaco Ruhrkohle/Ruhrchemie/ASTM fines leachate	negative	CHO-L	10 - 11%	9.0%
Texaco Ruhrkohle/Ruhrchemie/bioreactor effluent	negative	CHO-MD	20%	9.3 - 13%

^aSalmonella bacterial mutagenicity assay (*S. typhimurium*).

^bCHO - Chinese Hamster Ovary clonal toxicity assay; RAM - Rabbit alveolar macrophages toxicity assay; WI-38 - Human lung fibroblast cells; L - Low toxicity; M - Moderate toxicity; H - High toxicity;

MD - No detectable toxicity.

^c*Selenastrum capricornutum*, EC₅₀ - Concentration of effluent estimated to cause a 50% decrease in biomass.

^d*Pimephales promelas*, LC₅₀ - Concentration of effluent estimated to cause a 50% decrease in the fish population.

^eDashes mean parameter not analyzed.

^fValues expressed as percent concentration of sample in dilution water.

reduction of aqueous waste toxicity. This phenomenon also occurred with the biooxidation of Tezaco process quench condensates.

INTERNAL QUALITY CONTROL

The data compiled in this summary report originated from a series of Source Test and Evaluation projects conducted over a period of several years. During this time span the measurement techniques and quality control requirements were modified and evolved such that no single consistent set characterizes all of the data. The quality control procedures described below are generally applicable to these data types.

The internal quality control (QC) system for these data provided a set of routine internal procedures for assuring that the data output met prescribed criteria for data quality. Inherent and implied in this control function was a parallel function of measuring and defining the quality of data output. Generally, the internal QC procedures may be divided into two overlapping categories. One category includes those procedures which were used to control data quality within the prescribed limits of acceptability. These acceptability limits are usually related to data precision, accuracy, and completeness. The other category includes those procedures designed to provide a quantitative assessment of data quality, again in terms of precision, accuracy, and completeness. Some internal QC procedures, by their nature, fall into both categories.

Procedures Used for Control and Assessment of Data Quality

Procedures which serve both control and assessment functions include:

- replicate and repeat analyses (split samples),
- blank analyses,
- replicate samples,

- control samples,
- drift checks,
- spiked samples, and
- QA audits.

Procedures of this type were performed at a specified frequency, with a requirement that specific acceptance criteria be met prior to proceeding with sample analyses. Failure to meet prescribed acceptance criteria indicated the need for corrective action. By selecting appropriate acceptance criteria for QC results, the quality of the measurement data was effectively controlled within predetermined limits. Since precision and accuracy are most frequently the quality aspects which were being controlled, acceptance criteria for these types of procedures were defined in terms related to precision and accuracy. An essential part of the control function is the requirement that all acceptance criteria be met prior to proceeding with actual sample analyses. Table 14 is an example of a summary of internal QC requirements for the testing programs which includes designated frequencies and specific acceptance criteria for each procedure. In addition to controlling data quality within prescribed limits, the QC data provided the basis for assessing the performance of the measurement system.

TABLE 14. SUMMARY OF INTERNAL QUALITY CONTROL PROCEDURES FOR AQUEOUS SOLUTIONS

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Action or Corrective Action
Total Organic Carbon (TOC)	EPA/415.1	Method blank (DI water)	Prior to sample analyses	None	Used to indicate level of analytical contamination
		Control sample	1) Immediately following calibration 2) 10% (minimum 2) thereafter	Percent recovery between 85-115%	1) Repeat control sample analysis 2) Repeat calibration and sample analyses back to valid control sample analysis
		Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) $\leq 20\%$ for replicate determinations	Repeat duplicate analysis
		Impinger blank	Minimum 1	None	Will be used to determine amount of contamination
Total Inorganic Carbon (TIC)	Instrumental	Method blank (DI water)	Prior to sample analyses	None	Used to indicate level of analytical contamination
		Control sample	1) Immediately following calibration 2) 10% (minimum 2) thereafter	Percent recovery between 85-115%	1) Repeat control sample analysis 2) Repeat calibration and sample analyses back to last valid control sample analysis
		Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) $< 20\%$ for replicate determinations	Repeat duplicate analysis
Biochemical Oxygen Demand (BOD)	EPA/405.1				
Chemical Oxygen Demand (COD)	EPA/410.1	Method blank (DI water)	Prior to sample analyses	None	Used to indicate level of analytical contamination
		Control sample	10% (minimum 2)	Measure value within $\pm 15\%$ relative error (RE) of true value	1) Repeat control sample analysis 2) Repeat sample analyses back to last valid control sample analysis

(continued)

TABLE 14. (continued)

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Action or Corrective Action
Chemical Oxygen Demand (COD) (continued)		Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) <20% for replicate determinations	Repeat duplicate analysis
Total Dissolved Solids (TDS)	EPA/160.1	Method blank (DI water)	Prior to sample analyses	<5 mg residue	Used to indicate level of analytical contamination
		Control sample	10% (minimum 2)	Percent recovery between 90-110%	1) Repeat control sample analyses 2) Repeat sample analyses back to last valid control sample analysis
Total Suspended Solids (TSS)	EPA/160.2	Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) ≤20% for replicate determinations	Repeat duplicate analysis
		Method blank (DI water)	Prior to sample analyses	<5 mg residue	Used to indicate level of analytical contamination
		Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) ≤20% for replicate determinations	Repeat duplicate analysis
Total Alkalinity ($\text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^-$)	EPA/310.1	Control sample	Prior to sample analyses and at the conclusion of sample analyses	Measured value within ±1% relative error (RE) of true value	1) Repeat control sample analysis 2) Restandardize titrant, repeat analysis, control sample analysis
		Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) ≤20% for replicate determinations	Repeat duplicate analysis
Total Phosphate (PO_4^{3-})	Colorimetric	Method blank (DI water)	Prior to sample analyses	None	Used to determine analytical contamination
		Control sample	10% (minimum 2)	Measure value within ±20% relative error (RE) of true value	1) Repeat control sample analyses 2) Repeat sample analyses back to last valid control sample analysis

(continued)

TABLE 14. (continued)

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Action or Corrective Action
Total Phosphate (PO_4^{3-}) (continued)	Colorometric	Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) $\leq 20\%$ for replicate determinations	Repeat duplicate analysis
		Sample spikes	10% (minimum 1)	Spike recovery between 80-120%	Repeat analysis
		Method blank (DI water)	Prior to sample analyses	None	Used to determine analytical contamination
Chloride (Cl^-)	EPA/325.3	Control sample	10% (minimum 2)	Measure value within $\pm 20\%$ relative error (RE) of true value	1) Repeat control sample analyses 2) Repeat sample analyses back to last valid control sample analysis
		Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) $\leq 20\%$ for replicate determinations	Repeat duplicate analysis
		Sample spikes	10% (minimum 1)	Spike recovery between 80-120%	Repeat spike analysis
Na, Mg, Ca, K, Fe, Ag, Pb, Be, Cd, Cr, Cu, Ni, Ti, Zn	EPA/200.7	Instrument check standard	10% (minimum 1)	Measured value within $\pm 5\%$ of true value for elements of interest ($\pm 10\%$ for Ag)	Repeat calibration
		Calibration blank	10% (minimum 1)	Results within 2 standard deviations of mean for elements of interest	Repeat analysis (average 3 analyses)
		Interference check sample	10% (minimum 1)	Results within 1.5 times standard deviation of mean for elements of interest	Repeat calibration
		Sample spikes	10% (minimum 1)	Spike recovery between 80-120% for elements of interest for concentrations 5x detection limit	Repeat spike analysis

(continued)

TABLE 14. (continued)

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Action or Corrective Action
Na, Mg, Ca, K, Fe, Ag, B, Be, Cd, Cr, Cu, Ni, Ti, Zn (continued)	EPA/200.7	Duplicate analyses	10% (minimum 1)	Analyses agreement within 20% relative percent difference (RPD) for concentrations five times greater than detection limits	Repeat duplicate analysis
Sulfide (S^{2-}) and Thiosulfate ($S_2O_3^{2-}$) (onsite)	EPA/376.1	Digestion blank analysis	Prior to sample analyses	Less than 3 times detection limit	Determine source of contamination
		Minimum 1 of each impinger solution	None	Will be used to determine amount of contamination	
		Method blank	Daily	None	Used to determine analytical contamination
Sulfite (SO_3^{2-}) (onsite)	EPA/377.1	Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) $\leq$ 40% for replicate determinations	Perform replicate analyses on a different sample
		Method blank	Daily	None	Used to determine analytical contamination
		Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) $\leq$ 40% for replicate determinations	Perform replicate analysis on a different sample
Sulfate (SO_4^{2-})	EPA/375.3	Method blank (DI water)	Prior to sample analyses	None	Used to determine analytical contamination
		Control sample	10% (minimum 1)	Measured value within $\pm 20\%$ relative error (RE) of true value	Repeat control sample analyses
		Duplicate analyses	10% (minimum 1)	None	Report results
Total Sulfur	Oxidation/Gravimetric	Sample spikes	10% (minimum 1)	None	
		Method blank (DI water)	Prior to sample analyses	None	Used to determine analytical contamination

(continued)

TABLE 14. (continued)

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Action or Corrective Action
Total Sulfur (continued)	Oxidation/Gravimetric	Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) < 50% for replicate determinations	Repeat duplicate analysis
Ammonia (as NH_4^+) (onsite)	Standard Methods 417 A & D	Control sample	10% (minimum 1)	Percent recovery between 80-120%	Repeat control sample analysis
		Method blank	Daily	None	Used to determine analytical contamination
		Control sample	10% (minimum 2)	Measure value within $\pm 20\%$ relative error (RE) of true value	1) Repeat control sample analyses 2) Repeat sample analyses back to last valid control sample analysis
		Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) $\leq 20\%$ for replicate determinations at concentrations greater than 5 times detection limit	1) Perform replicate analysis on a different sample 2) Repeat sample analyses back to last valid replicate analyses
Total Cyanide (CN) and Thiocyanide (SCN^-) (onsite)	Colorimetric	Sample spikes	10% (minimum 1)	Spike recovery between 80-120%	1) Spike a different sample and analyze 2) Repeat sample analyses back to last valid spike recovery
		Impinger blank	Minimum of 1	None	Used to determine analytical contamination
		Method blank	Daily	None	Used to determine analytical contamination
		Control sample	10% (minimum 1)	Measure value within $\pm 20\%$ relative error (RE) of true value	1) Repeat control sample analyses 2) Repeat sample analyses back to last valid control sample analysis
		Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) $\leq 40\%$ for replicate determinations	Perform replicate analysis on a different sample
		Sample spikes	10% (minimum 1)	Spike recovery between 80-120%	Spike a different sample and analyze

(continued)

TABLE 14. (continued)

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Action or Corrective Action
Total Cyanide (continued)		Impinger blank	Minimum 1	None	Will be used to determine amount of contamination
Total Phenolics	EPA/420.1	Method blank	Prior to sample analyses	None	Used to determine analytical contamination
		Control sample	10% (minimum 1)	Measure value within $\pm 15\%$ relative error (RE) of true value	1) Repeat control sample analyses 2) Repeat sample analyses back to last valid control sample analysis
		Duplicate analyses	10% (minimum 1)	Relative percent difference (RPD) $\leq 20\%$ for replicate determinations	Repeat duplicate analysis
		Sample spikes	10% (minimum 1)	Spike recovery between 80-120%	Repeat spike analysis
		Impinger blank	Minimum 1	None	Will be used to determine amount of contamination
As, Hg, Pb, Sb, Se	Atomic Absorption	Calibration blank	Prior to sample analyses	None	Used to indicate level of analytical contamination
		Digestion blank	Prior to analysis	Less than three times detection limits	Determine source of contamination and reinject
		Control sample	1) Immediately following calibration 2) 10% (minimum 2) thereafter	Measured value within $\pm 15\%$ of true value	1) Repeat analysis 2) Repeat calibration
As, Hg, Pb, Sb, Se		Mid-level standard than 20 samples	1 in 20 if more than 20 samples analyzed	Response within $\pm 10\%$ of original calibration curve	Repeat calibration
		Duplicate digestion and analyses	10% (minimum 1)	Relative percent difference (RPD) $\leq 20\%$ for replicate determinations for concentrations greater than five times detection limit	Repeat duplicate analyses

(continued)

TABLE 14. (continued)

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Action or Corrective Action
As, Hg, Pb, Sb, Se	Mid-level standard	Sample spikes	10% (minimum 1)	Spike recovery between 80-120% for elements of interest	Repeat spike analysis
		Impinger blank	Minimum 1	None	Will be used to determine sources of contamination
U, Th		Performed by contract laboratory	Will rely on contract lab QA/QC procedures		
		Duplicate analyses	One	None	Report results

SECTION 5

IMPACT OF GASIFICATION PROCESS ON QUENCH CONDENSATE QUALITY

INTRODUCTION

The gasification of coal produces large quantities of liquid effluents. Gasification subjects coal to varying degrees of thermal treatment using a combination of steam and oxygen or air. Steam is used in excess and serves as both a reactant and temperature moderator. Removal of excess steam from the raw product gas also removes condensible hydrocarbons and water soluble contaminants. These condensates represent the major wastewater source in coal gasification.

Coal gasification processes are usually divided into two general classifications with respect to levels of organic contamination in process condensates: those processes that produce little or no phenolics, oils, and tars and those processes that produce substantial quantities of these pollutants. Among processes producing organic contaminants, a further division may be made between those that are significant producers of tars and heavy oils and those that are not.

VARIABILITY OF QUENCH CONDENSATE PRODUCTION WITH GASIFICATION PROCESS

Few data are available regarding the quantity of process condensate produced during commercial-scale coal gasification and the associated variability that characterizes individual water soluble pollutants (e.g., phenols, ammonia, hydrogen sulfide, hydrogen cyanide). Pilot studies with coal gasification process development units (PDUs) have produced the majority of the available data regarding process wastewater characteristics and the

variability of wastewater parameters. However, some wastewater production data are available for commercial gasifiers, and these data are summarized in Table 15. This table shows the normalized production rate of process condensate and selected gasifier pollutants for the Lurgi, Texaco, and Koppers-Totzek processes (5,11,23). The information was assembled during test burns with American coals. These data serve to emphasize the difference between the high and low tar, oil, and phenol producers both with respect to the quantity of quench condensate produced and the characteristic quality.

In the case of the Lurgi fixed-bed gasifier, there appears to be some relationship between coal-type and the quantity of quench liquor generated during coal gasification. However, the amount of process wastewater generated may also be dependent on the quantity of steam consumed during thermal treatment. The data also indicate that the smaller the particle size of the feed coal, the lower the apparent steam requirement for gasification and the subsequent amount of quench liquor generated. It is important to note that the quantity of tar, oil, and phenol produced in the Lurgi gasifier does not appear to be coal dependent. However, there would be significant differences in the concentrations of these pollutants between the various coal-types because of differences in quench liquor volumes.

Testing with the Synthane PDU has shown that the production of quench condensate and associated condensible hydrocarbons and water soluble contaminants is extremely sensitive to changes in gasifier process variables (e.g., the method of coal injection and the source of oxygen used for thermal treatment). Significant variations in tar, oil, and phenol production occur during transient operating periods (i.e., start-up or shutdown), and between steady state operations at different gasifier operating conditions (24).

An increase in the degree of gas-solid contact, the reaction temperature, and the residence time of the devolatilized species in the gasifier hot zone will reduce the organic contamination level in the quench condensates. Near complete extinction of these compounds is possible by providing the

TABLE 15. NORMALIZED PRODUCTION OF QUENCH LIQUORS/GAS COOLING CONDENSATES

Gasifier	Coal	Wastewater Produced kg water/ kg coal	Steam Consumed kg steam/ kg coal	Tar/Oil Produced kg T-O/ kg coal	Phenols Produced kg C ₆ H ₅ OH/ kg coal
Lurgi ^a	Montana Rosebud ^b	1.0	1.25	0.04	0.004
	Illinois #6 ^b	2.1	2.51	0.03	0.005
	Illinois #5 ^b	1.8	2.25	0.05	0.005
	Pittsburgh #8 ^b	2.6	3.24	0.05	0.004
	Montana Rosebud ^c	0.9	1.01	0.04	0.005
Texaco ^d	Illinois #6 ^e	0.7-1.3	0.78 ^f	8	8
Koppers-Totzek ^h	Illinois #6 ^e	0.9	NA ⁱ	8	8

^aLurgi gasifier at Westfield, Scotland.^bCoarse graded (6-32 mm).^cFine graded (2-10 mm).^dMährische/maische in Oberhausen-Holten, Federal Republic of Germany.^ePulverized (<2 mm).^fSteam flow rate is taken as the sum of fresh makeup slurry water, coal moisture, and water in additives and flocculants.^gNegligible.^hTVA projections (22).ⁱNA = data not available.

appropriate combination of coal devolatilization conditions and product gas residence time (25). Phenol production is stable regardless of differences in devolatilization conditions. However, phenol is subject to thermal decomposition at gasification temperatures in excess of 700°C (26). Heavy hydrocarbon formation is extremely sensitive to devolatilization conditions.

Fixed-Bed Coal Gasification

Results obtained from the analysis of quench condensates from an oxygen-blown, lignite-fired Lurgi-type gasifier; an air-blown, bituminous-fired Chapman gasifier; and a by-product coke plant are presented in Table 16 (27,28). These data show that similarities exist between the qualities of the two fixed-bed gasifier quench condensates. This similarity extends to both the type and concentration of certain key organic contaminants (e.g., phenol, cresols, and dimethylphenols). The apparent higher pollutant concentrations in the Chapman process wastewater are a result of gas liquor recirculation to the gas scrubbers. Other variables are coal-type, oxygen source, bed temperature, gas/solid contacting, and gas and solid residence times.

There are significant differences between the composition of noncaking (e.g., North Dakota lignite) and caking (e.g., Illinois No. 6) coals. The carbon, oxygen, sulfur, and moisture contents are different for the coal-types which should influence waste effluent quality. Studies with the Synthane PDU produced increased tar and thiocyanate levels in quench condensates when caking coals were gasified. However, phenol levels were unaffected by coal-type (26). The impact of coal-type on the concentration of cyanide and ammonia in quench condensates is not well documented. Similar studies with steam-oxygen and steam-air gasification indicated that only tar, phenol, and cyanide production levels were statistically different for the two oxygen sources (see Appendix B).

Studies with the Synthane PDU indicated that quench condensate pollutant levels were greatly reduced when the gasifier feed coal injection geometry was

TABLE 16. WASTEWATER CHARACTERISTICS FOR THREE COAL CONVERSION
PROCESS CONDENSATES

Water Quality Parameters (mg/L)	Process Condensates		
	Lurgi-type at Kosovo	Chapman	By-Product Coke
BOD	12,200	15,900	3,420
COD	20,200	28,500 $\pm$ 1,100 ^a	4,860 $\pm$ 390
TOC	6,490	9,430	6,160
NH ₃ -Nitrogen	4,340	8,130 $\pm$ 90	2,850
Total Kjeldahl Nitrogen	4,010	9,420	3,160
Nitrate-Nitrogen	<0.5	<0.5	<0.5
Total Phosphate-Phosphorous	0.12	5.48	0.21
Total Acid Hydrolysable Phosphate-Phosphorous	0.08	5.48	0.21
Total Phenolics	3,030	2,130 $\pm$ 110	1,140
Phenol Speciation			
Phenol	1,740 $\pm$ 100	1,460 $\pm$ 170	888 $\pm$ 52
o-Cresol	406 $\pm$ 27	420 $\pm$ 54	70.0 $\pm$ 2.3
m&p-Cresol	1,040 $\pm$ 60	1,120 $\pm$ 120	279 $\pm$ 14
2,6-Dimethylphenol	33.1 $\pm$ 10.0	19.1 $\pm$ 0.2	2.2 $\pm$ 1.0
2,4-Dimethylphenol	172 $\pm$ 17	196 $\pm$ 27	14.5 $\pm$ 0.1
3,5-Dimethylphenol	266 $\pm$ 21	172 $\pm$ 24	23.4 $\pm$ 0.8
3,4-Dimethylphenol	271 $\pm$ 24	681 $\pm$ 82	41.5 $\pm$ 1.3
1&2-Naphthol	13.0 $\pm$ 30.6	14.5 $\pm$ 0.3	4.5
p-Phenylphenol	<10 ⁻²	<10 ⁻²	<10 ⁻²
Oil and Grease	917	540	700
Cyanide	<0.02	59 $\pm$ 1	69 $\pm$ 1
Thiocyanate	83	1,430	570
Sulfide	<10	207 $\pm$ 12	241 $\pm$ 18
TDS	2,010	48,600	4,870
TVDS	1,890	42,300	4,700
TSS	417	11	20
TVSS	402	11	18

^aAverage $\pm$ one standard deviation from the mean.

Reference: (27).

altered from free fall to deep bed-injection (see Appendix B). The tar, phenol, COD, and TOC wastewater pollutant levels were reduced by factors of 10 to 50 times the free fall production rates (26). This indicates that gasifier process variables (e.g., gas-solid contacting, mean reaction temperature, and gas-solid residence time) are altered when the point of feed coal injection is shifted.

The chemistry of the Lurgi-type and Chapman quench condensates were compared to process condensates from by-product coke production. Although coal coking consists of the pyrolysis of coal at temperatures approaching 1000°C in the absence of oxygen, it produces gas condensates that are similar in composition to fixed-bed coal gasification gas liquors. During coking volatile components are driven from the coal, collected, and condensed. Tar is decanted from the condensate, and the resultant liquor is termed flushing liquor or waste ammonia liquor. This liquor is the major source of wastewater in coke production.

Although coal conversion effluents laden with organic contaminants contain components similar to coke plant wastewater, the data in Table 15 show differences in concentrations and relative proportions. For example, the fixed-bed gasification quench condensates have higher concentrations of BOD, COD, and phenolics than coke plant quench condensates. Gasification process wastewaters also are higher in ammonia, although coke plant gas liquor may be higher in cyanide and possibly thiocyanate than fixed-bed gasification quench waters. Definitive comparisons of cyanide data are difficult because of problems with cyanide preservation and analysis in coal gasification wastewaters. Chemical interactions between cyanide and reduced sulfur species may account for some loss of cyanide in unpreserved samples.

Entrained-Bed Coal Gasification

The presence of organic contaminants in quench condensates produced during coal gasification is related to the physical configuration of the

gasifier and its operating conditions. Processes tending to show little or no organic contamination may be either entrained flow or ash-agglomerating fluidized-bed gasifiers that operate at temperatures greater than 1000°C and produce ash as slag or agglomerates. Examples of such processes are the Texaco, Koppers-Totzek, and KRW gasifiers. Gasifiers that yield condensates free of organic contamination are characterized by small coal particle size and extensive gas-solids mixing. The cocurrent flow of gas and coal in entrained-bed gasifiers permits the transport of devolatilized organics with the product gas through the oxidation zone rather than leaving the gasifier without passing through this zone as is the case with fixed-bed gasifiers. Data showing the quench liquor/process condensate stream qualities for the Texaco and Koppers-Totzek gasifiers are assembled in Table 17 (11,23). These wastewater quality data are characteristic of the gasification of bituminous coals with similar carbon, sulfur, and ash levels. The Koppers-Totzek gasifier is a commercial level technology; however, the test data should be considered indicative of a demonstration process because the coal used during the test burn was not normally gasified at the Ptolemais facility. The Texaco facility is a demonstration level technology.

The wastewater quality data for the Texaco process were obtained during a test run at the Ruhrkohle/Ruhrchemie Gasification Plant at Oberhausen-Holtien, Federal Republic of Germany. The Texaco Coal Gasification Process is a pressurized, entrained-bed, down-flow slagging gasifier. It operates under pressures of 2 to 8 MPa and at elevated temperatures, generally in the range of 1200 to 1500°C. These temperatures are above the melting point of the coal ash. The Koppers-Totzek process is also an entrained-bed gasifier. However, the Koppers-Totzek gasifier operates at atmospheric pressure and at temperatures between 1400 and 1600°C. Both processes gasify pulverized coal in an entrained-bed reactor, using oxygen and steam as gasification media. The wastewater quality data for the Koppers-Totzek process were projected by TVA based on a test run at the Nitrogenous Fertilizer Industry plant in Ptolemais, Greece. Both gasifiers conducted tests with an Illinois Number 6 coal.

TABLE 17. COMPARISON OF WASTEWATERS FROM ENTRAINED-BED GASIFIERS PROCESSING BITUMINOUS COALS^a

Parameter	Texaco Gasifier ^b Ruhrkohle/Ruhrchemie Pilot Plant	Koppers-Totzek Gasifier ^c	
		Range	Average
pH standard units	8.3	- ^d	7
Total Alkalinity as CaCO ₃	4,550	-	-
Chemical Oxygen Demand(s) ^e	216	-	-
Ammonia-Nitrogen	1,640	166-270	270
Sulfide	66	-	1
Sulfite	84	34-71	51
Sulfate	38	349-772	520
Thiocyanate	49	5.5-11	8
Cyanide	29	9.6-53	14
Chloride	802	-	289
Fluoride	59	8-63	49
Formate	359	-	-
Boron	76	3-30	20

^aAll units in mg/L except where noted.

^bIllinois #6, HHV=12,686 BTU/lb, 70.94% carbon, 3.37% sulfur, 11.21% ash (11).

^cIllinois #6, Amax Delta mine. Tennessee Valley Authority projections based on data from the Ptolemais Greece Koppers-Totzek Gasifier (22).

^dDashes denote no data available.

^e(s) = soluble.

The Texaco quench condensates contain higher concentrations of ammonia, cyanide, and alkalinity than the Koppers-Totzek gas liquors. In general, entrained-bed gasifiers convert the least amount of coal nitrogen to NH_3 and HCN because of their elevated operating temperatures (24). The distribution of ammonia and cyanide through downstream processing equipment is influenced by the operation of the gas quench system. Both ammonia and hydrogen cyanide are soluble in water and their capture is influenced by quench system pH (24). Ammonia removal in the quench can be enhanced by a lowered pH in the scrubber liquor, but removal of HCN will be reduced as would H_2S .

Formate appears to be a significant pollutant in the quench condensates from the Texaco process and may be characteristic of the high operating pressures of this gasifier. For the most part, light hydrocarbons and traces of C_6 hydrocarbons (i.e., aerosols and volatile compounds such as benzene) will pass through the quench and enter the acid-gas removal system.

Both the Texaco and Koppers-Totzek quench condensates are relatively low in thiocyanate, sulfide, and chemical oxygen demand. Hydrogen sulfide will be partially removed during cooling of the raw product gas. The degree of partitioning depends upon such variables as condensate recycle ratio, pH, and the composition of the gas liquor. The absorption of sulfur species is dependent on the efficiency of gas/liquid contacting and is strongly influenced by the mass transfer characteristics of the quench system (24).

Both the Texaco and Koppers-Totzek quench condensates are high in chloride, fluoride, and boron. In general, all chlorine and fluorine that is volatilized during gasification should be removed in the quench system. The presence of elevated concentrations of boron in the quench condensates is characteristic of the entrained-bed gasification process which uses an ash/water separation operation prior to blowdown of the gas liquor to wastewater treatment. This process permits greater contact between quench condensates and the fine slag or ash agglomerates which enhances the mass transfer of trace elements into the liquid phase. Similar observations were

reported during pilot-scale testing of another high temperature, high pressure, entrained flow gasifier (29).

The difference in the concentration of chloride, fluoride, and boron in quench condensates from the Texaco and Koppers-Totzek gasifiers is probably a coal dependent phenomenon. It is emphasized, however, that the production and distribution of trace elements during coal gasification is one of the least understood areas in environmental characterization. Consequently, no attempt is made to assess the differences in light of known gasification process characteristics.

SECTION 6

BIOOXIDATION OF COAL CONVERSION WASTEWATERS

INTRODUCTION

Wastewater bioassay data indicated that biooxidation treatment of tar producing and non-tar producing coal gasification wastewaters effects a substantial degree of improvement toward the reduction of aqueous waste toxicity (see Section 4.0). Pretreated (i.e., solvent extracted and/or steam stripped) wastewaters from either the Texaco or Lurgi coal gasification processes showed a reduced toxicity after activated sludge treatment when tested with the in vitro cytotoxicity, fresh water alga, and fathead minnow assays. These data would suggest that the potential adverse ecological impacts that may result from the discharge of coal gasification wastewater can be reduced with biooxidation treatment. Such treatments as the activated sludge, rotating biological contactor, and aerated lagoon processes may be needed to produce acceptable effluents for discharge. This section discusses the feasibility of using biological treatment to improve the water quality of coal conversion effluents.

In order to assess the feasibility of using biological processes for the treatment of coal conversion wastewaters, it is necessary to determine if the constituents of the wastewaters are biologically treatable. Of the many organic compounds that characterize fixed-bed gasifier wastewaters, only phenolics degradation has been extensively investigated. However, review of this work should provide information about the microbial degradation of other aromatic compounds because phenols are major intermediates in the degradation of most aromatics.

Biological oxidation of coke plant effluents using acclimated microorganisms has provided the basis for much of the research into biooxidation of fixed-bed gasifier quench condensate. The early studies with the biodegradation of coal conversion wastewater were often based on the treatment of diluted raw gasifier quench condensate without specification of practicable pretreatment requirements. In these studies the attainment of steady-state operation was based on mean bacterial cell residence time rather than hydraulic residence time. That is, once feed conditions and operating parameters were established for a bioreactor, it was operated for a period equal to three sludge wasting cycles prior to performance data collection.

Much of the published data on biooxidation are for the treatment of process development unit (PDU) coal conversion wastewaters. Information on the biooxidation of commercial-scale gasification process wastewaters is largely of the verification study type. That is, large bench-scale or pilot facilities were operated to develop performance data exclusive of a basis-of-design. As a consequence, the performances of these systems were not optimized and design parameters were not developed.

Three studies which examined the treatment of commercial-scale gasification quench condensates are examined in this section. These studies established the feasibility of using biooxidation treatment for removal of pollutants from fixed-bed and entrained-bed gasifier quench condensates. The gasifiers examined were the Chapman, Lurgi, and Texaco processes (30,7,11).

WASTEWATER QUALITY VARIABILITY

Wastewaters from coal conversion processes can originate from a variety of sources depending upon the specific processes employed. The composition of the wastewater depends upon the process technology, operating conditions, and nature of the feed coal. These factors impact upon wastewater quality variability which, in turn, affects biooxidation treatment performance. Data are not available which adequately characterize pollutant variability in

commercial-scale coal gasification wastewaters. However, several studies provide data on bulk sample wastewater quality that can be used to assess short-term aqueous waste variability associated with fixed-bed gasification processes. Process wastewaters, which will be referred to in this section as gas liquor, were characterized for both the Chapman and Lurgi gasifiers (7, 30). The Chapman study involved the collection of gas liquor samples before tar/oil separation over a year of gasifier operation, while the Lurgi study collected bulk samples of pretreated gas liquor during a test run with American coal. The Lurgi gas liquors were pretreated by tar/oil separation, filtration, phenol recovery by solvent extraction, and steam stripping for ammonia and acid gas removal. Both gasifiers processed Eastern United States bituminous coals.

Wastewater variability data for Chapman gas liquors are presented in Table 18. These quality data are similar to other raw gas liquors from fixed-bed gasifiers in that the samples contain elevated concentrations of phenols, grease and oil, thiocyanate, ammonia, and reduced sulfur compounds. These gas liquors are high in oxygen demand-producing substances and have significant amounts of dissolved solids. The Chapman gas liquors show wide variations in the quality data for each pollutant. Part of this variability may be due to nonsteady-state gasifier operation or non-representative sample collection. The limited data base for certain key pollutants prevents calculation of raw waste load variability factors for this gasification process. However, data for the concentration of biochemical oxygen demand, ammonia, and thiocyanate present in Chapman gasification quench condensates indicate that these waters are characterized by substantial quality variability during normal gasifier operation.

Wastewater characterization data for Lurgi gas liquors pretreated for phenols, ammonia, and acid gas removal are presented in Table 19. These data characterize a wastewater of much less pollutant variability and lower strength which results from the removal of phenolics and ammonia. Pollutants remaining after pretreatment are non-phenolic organic carbon, organic

TABLE 18. WASTEWATER VARIABILITY CHARACTERISTICS OF THE CHAPMAN GASIFIER^a

Parameter	Number Observations	Concentration ^b		
		Average ^c	Standard Deviation	Range
Alkalinity as CaCO ₃	29	1,631	153	1,362-2,008
Biochemical Oxygen Demand	31	7,581	2,561	3,640-14,130
Total Organic Carbon	3	32,777	33,102	13,600-71,000
Chemical Oxygen Demand	4	30,009	14,026	19,500-49,132
Phenols	6	1,924	272	1,700-2,410
Grease and Oil	8	2,537	2,059	624-6,535
Thiocyanate	12	613	251	160-922
Sulfide	5	5,376	3,784	829-8,857
Ammonia-Nitrogen	21	3,201	1,470	1,907-7,812
pH, standard units	32	7.9	NA	6.9-8.3
Total Residue	5	19,060	5,733	14,780-28,350

^aHolston Army Ammunition Plant in Kingsport, Tennessee.

^bUnits are mg/L unless otherwise noted.

^cAverage of grab samples collected over a year's operation.

Reference: (30).

TABLE 19. PRETREATED LURGI GAS LIQUOR WASTEWATER CHARACTERIZATION^a

Parameter	Mean	Standard Deviation	High	Low	Number of Data Points
Soluble, Chemical Oxygen Demand, mg/L	822	28	854	736	15
Total Organic Carbon, mg/L	270	47	380	195	15
Total Kjeldahl Nitrogen, mg/L	392	7	404	377	15
Ammonia Nitrogen, mg/L	277	63	385	152	15
Nitrate Nitrogen, mg/L	0.95	0.37	1.6	0.03	13
Cyanide, mg/L	0.99	0.56	1.9	0.22	15
Thiocyanate, mg/L	142	20	203	120	15
Phenols, mg/L	1.03	0.16	1.4	0.8	15
Total Phosphorus, mg/L	0.21	0.05	0.35	0.13	15
Fluoride, mg/L	40	2.2	45.4	37	15
Specific Conductance at 25°C (mhos/cm)	2,868	43	2,944	2,790	15
pH (standard units)	7.7	0.2	8.1	7.4	15

^aGas Liquor in drums shipped from the Lurgi facility at Sasolburg, South Africa.

Reference: (7).

nitrogen, ammonia, and thiocyanate, all of which are biodegradable or subject to microbial transformations that would reduce their strength.

BIOOXIDATION STUDIES

Effects of Dilution

Coal conversion process wastewater biological oxidation kinetic constants and operational parameters are compared in Table 20 (30,31,32). Most of these studies are for the treatment of PDU gas liquors after pretreatment for ammonia reduction by air stripping and/or dilution with tap water or sewage. It was found that fixed-bed gasifier wastewater could not be biotreated at full strength without substantial phenolic reduction to concentrations below 1000 mg/L. Generally, biooxidation of high phenolic gas liquors (2000-3000 mg/L) produced relatively high concentrations of effluent volatile suspended solids which resulted from the bulking of the activated sludges during settling. It was concluded from these studies that long-term process stability could not be sustained when treating gas liquor at 50% strength (i.e., one part gas liquor in one part water) and high phenolic loadings. This conclusion resulted from a series of tests where feed strength and loading were varied independently in sequential and parallel experiments. Factors which impose limitations on feed wastewater strength are not completely understood; however, the presence of inhibitory organic compounds is suspected.

These studies did not attempt to ascertain minimum dilution requirements. The GFETC gas liquor at 33% strength contained COD levels between 5000 and 7000 mg/L, which equates to substrate removal rates in milligrams COD removed per milligram mixed liquor volatile suspended solids under aeration per day of 0.2 to 0.5. This is one of the highest reported organic contaminant levels for coal conversion wastewaters ever treated by the activated sludge process. It has been found that an activated sludge process exhibits long-term

TABLE 20. COAL CONVERSION WASTEWATER BIOOXIDATION PROCESS DESIGN PARAMETERS

Parameter	GFETC ^a	Hygas ^b	Synthane ^c	NETC ^d	Chapman ^e
Pretreated influent concentration (I)	33	100	15	36-40	5
Reactor pH (standard units)	7.0-7.5	7.0-7.5	— ^f	6.2-7.4	7.1-7.7
Loading (mg COD [BOD] applied/mg MLVSS-day)	0.25-0.58 [0.15-0.34]	0.43-1.29 [0.32-0.95]	— —	— [0.38-0.64]	— —
Substrate removal rate (mg COD [BOD] removed/mg MLVSS-day)	0.21-0.48 [0.14-0.32]	0.36-1.02 [0.29-0.82]	— [0.2-0.6]	— [0.35-0.60]	— [0.03-0.21]
Mean cell residence time (days)	10-40	10-40	5.5-38	4.4-11	4-58
Hydraulic residence time (days)	9.1-21.6	2.05-2.98	1.0	0.6-2.2	0.7-3.3
Yield coefficient, COD basis [BOD basis]	0.29 [0.43]	0.10 [0.14]	— [3.7]	— [0.54]	— [0.09]
Decay coefficient, days ⁻¹ , COD basis [BOD basis]	0.038 [0.037]	0.01 [0.02]	— [0.033]	— [0.09]	— [0.083]
Oxygen utilization coefficient (mg O ₂ /mg COD [BOD] removed)	0.77 [1.0]	0.30 [0.36]	0.56 [0.75]	— [0.30]	— —
Oxygen utilization coefficient (mg O ₂ /mg MLVSS-day) COD basis [BOD basis]	0.01 [0.05]	0.06 [0.05]	0.09 [0.11]	— [0.08]	— —

^aGFETC = pilot-plant operated by the Grand Forks Energy Technology Center; now part of University of North Dakota Energy Research Center.

^bPilot-plant operated by the IGT Process Research Division.

^cPilot-plant operated by the Pittsburgh Energy Technology Center.

^dPilot-plant operated by the Morgantown Energy Technology Center.

^eEast Tennessee State University.

^fDash means data not available.

References: (30,31).

operational stability when the following minimum bioreactor effluent quality characteristics are maintained:

- Phenolics in reactor less than 2 mg/L,
- Thiocyanates in reactor less than 10 mg/L,
- COD reduction greater than 70 percent, and
- Effluent solids loss less than 100 mg/L.

It has been found in studies with Synthane, Chapman, Hygas, and GFETC wastewaters that bioreactors which operate at long mean cell residence times (10 to 40 days) exhibit the most consistent pollutant removal efficiencies. Such an operating condition corresponds to a low specific substrate removal rate. Under these conditions, bioreactor effluent pollutant levels are not especially sensitive to substrate loading (i.e., pollutants subject to microbial transformations).

Effects of Pretreatment

Activated sludge treatment tests with pretreated gas liquors from the Texaco and Lurgi processes were conducted in order to develop effluent characterization data for discharge permits (7,11). These studies did not determine biological oxidation kinetic constants and operational parameters because they were designed to produce data in support of discharge permit applications. (Some limited test data for the kinetics of biochemical oxidation are available for Texaco gas liquors. However, these data are suspect because they were taken from a gross correlation based on limited testing.)

Performance data for the biooxidation of Texaco and Lurgi gas liquors are presented in Table 21. Since both of the pretreated gas liquors are low in ammonia, the principal concerns of the biooxidation process are removal of biodegradable organic carbon and thiocyanates. Pretreated gas liquors from

TABLE 21. PERFORMANCE DATA FOR ACTIVATED SLUDGE TREATMENT OF COAL CONVERSION WASTEWATERS^a

Parameter	Texaco-Ruhrkohle/ Ruhrchemie ^b		Lurgi- Sasolburg ^c	
	Influent	Effluent	Influent	Effluent
BOD ₅ (total)	200	14	NA ^d	NA
BOD ₅ (soluble)	NA	4	487	8
COD (total)	311	73	NA	NA
COD (soluble)	NA	50	1,087	157
Phenol (total)	NA	NA	43	0.16
TKN	34	21	121	102
NH ₃ -N	21	13	61	84
NO ₃ -N	0.23	3.6	0.62	9.44
CN ⁻	0.11	0.07	0.4	0.23
SCN ⁻	3.6	<3.0	143	3
S ⁼	43	<1.0	NA	NA
TDS	960	11,300 ^e	3,143	3,241
TSS	50	18	18	33
VSS	18	13	15	28
Alkalinity (as CaCO ₃)	2,381	1,539	226	154
pH (standard units)	7.1	8.5	7.7	7.6

^aData are averages of single analyses performed at various frequencies during the test periods and are expressed as mg/L, except where noted.

^bWastewaters pretreated by sedimentation, air stripping, and neutralization.

^cWastewaters pretreated by tar-oil separation, filtration, phenol recovery by solvent extraction, steam stripping, and air stripping after lime pretreatment.

^dNA means data not available.

^eHigh TDS is the result of the addition of NaOH and H₂SO₄ during pretreatment.

the Texaco process are substantially lower in BOD and COD than quench condensates produced by the Lurgi gasifier, even after these wastewaters were treated for phenolics removal. The Lurgi wastewaters were higher in ammonia, organic nitrogen, thiocyanate, and phenol than the Texaco gas liquor. However, the Texaco wastewater had a substantially higher alkalinity than the pretreated Lurgi gas liquor.

The bioreactor treating Lurgi wastewater was operated at a sludge age of approximately 60 days and a hydraulic residence time of 24 hours. The Texaco wastewater bioreactor operating conditions were not defined. Both systems were effective for the removal of BOD and COD from their respective gas liquors. However, only a small degree of biological nitrification occurred in each bioreactor, suggesting the presence of some inhibitory pollutant or pollutants in each wastewater. The operational pH of the Texaco bioreactor mixed liquor was probably too high for effective thiocyanate degradation, and may have resulted in some free ammonia toxicity to the nitrifiers. Both treatment systems were effective for the removal of biodegradable organic carbon. The Lurgi bioreactor was also effective for the removal of thiocyanate from fixed-bed gas liquor. In general, these data indicate that pretreated gas liquors from both fixed-bed and entrained-bed gasifiers can be effectively treated by biooxidation.

SECTION 7

IMPACT OF COAL GASIFICATION WASTEWATER DISCHARGES

INTRODUCTION

This analysis has as its focus the compilation of numerous source test and evaluation study data on potentially hazardous substances in coal gasification wastewaters. Since the data represent various gasifiers, coal types, operating conditions, and configurations and since the effluents are variable in their physical and chemical nature, a systematic approach was needed to place the data on a common basis for comparison. Much of the data developed from the environmental characterization sampling programs did not yield wastewater quality data for the different gasification processes that were directly comparable because they were designed to focus on streams of potential environmental significance. However, these environmental characterization test programs did provide a listing of pollutants common of the different coal gasification processes, and these data were used to select wastewater discharge pollutants for environmental monitoring. This section will address the nature of these pollutants and their environmental significance.

WASTEWATER DISCHARGE POLLUTANTS

The heterogeneous nature of coal gives rise to a wide variety of organic and inorganic compounds in aqueous streams resulting from coal conversion processes. These pollutants are summarized in Tables 22 and 23 for the fixed-bed (20,21) and entrained-bed gasification processes, respectively.

TABLE 22. SUBSTANCES IDENTIFIED IN FIXED-BED GASIFICATION WASTEWATERS

Lurgi ^a Gas Liquor	Chapman ^b Separator Liquor	Wellman-Galusha ^c Ash Sluice Water
Aluminum	Ammonia	Ammonia
Ammonia	Antimony	Barium
Antimony	Arsenic	Benzenethiol
Arsenic	Barium	Benzo(e)pyrene
Barium	Boron	Chromium
Beryllium	Cadmium	Cresols
Boron	Calcium	Cyanide
Calcium	Carboxylic Acids	Dibenz(a,h)pyrene
Catechols	Cerium	Iron
Cerium	Cesium	Lanthanum
Chromium	Chloride	Lithium
Copper	Chlorine	Phenols
Cobalt	Copper	Selenium
Cresols	Cyanide	Thiocyanate
Cyanide	Fluorine	
Fluorine	Fused Aromatic Hydrocarbons	
Iron	Heterocyclic Nitrogens	
Lead	Heterocyclic Sulfurs	
Lithium	Iron	
Magnesium	Lanthanum	
Manganese	Lithium	
Mercury	Magnesium	
Molybdenum	Mercury	
Nickel	Phenols	
Phenol	Phosphorus	
Phosphorus	Rubidium	
Resourcinols	Scandium	
Rubidium	Selenium	
Scandium	Silicon	
Selenium	Silver	
Silicon	Thiols	
Silver	Titanium	
Sodium	Tungsten	
Strontium	Yttrium	
Thiocyanate	Zirconium	
Titanium		
Uranium		
Vanadium		
Xylenols		
Yttrium		
Zinc		
Zirconium		

^aFor various coals (e.g., bituminous and lignite).^bVirginia bituminous coal.^cPennsylvania anthracite.

References: (1,2,4,6,14,20).

TABLE 23. SUBSTANCES IDENTIFIED IN ENTRAINED-BED GASIFICATION WASTEWATERS

Koppers-Totzek Modderfontein	Texaco Ruhrkohle/Ruhrchemie
Ammonia ^a	Ammonia
Anthracene ^b	Barium
Barium ^b	Boron
Benz(a)anthracene ^b	Bromine
Benzo(b)fluoranthrene ^b	Cerium
Boron ^a	Chlorine
Bromine ^b	Cyanide
Chlorine ^a	Fluorine
Copper ^b	Iron
Crysene ^b	Lead
Cyanide ^a	Magnesium
Fluoranthene ^b	Molybdenum
Fluorine ^{b,c}	Nickel
Iron ^{b,c}	Potassium
Magnesium ^{b,c}	Silicon
Nickel ^b	Sodium
Phenanthrene ^b	Thiocyanate
Potassium ^{b,c}	Zinc
Pyrene ^b	Zirconium
Silicon ^a	
Sodium ^c	
Thiocyanate ^a	
Zinc ^c	

^a Quench condensates.

^b Rectisol wastewater.

^c Compressor condensates.

References: (10,11,13).

These aqueous phase pollutants are characteristic of wastewaters from the Wellman-Galusha, Chapman, Lurgi-type, Texaco, and Koppers-Totzek gasifiers. Many of the substances listed in Tables 22 and 23 were detected and are typically present in coal gasification wastewaters, albeit at relatively low concentrations.

Process condensates from coal gasification have long had a reputation for being highly polluting and difficult to treat because they contain substantial concentrations of ammonia, phenols, and sulfur compounds. All of these chemicals can be directly toxic to aquatic life. They also exert an indirect toxic effect, as they undergo biochemical oxidation in the aquatic environment which consequently becomes deficient in dissolved oxygen.

Pollutants in aqueous wastes from coal gasification processes representing the highest potential for environmental (ecological) hazard are ammonia, cyanide, and phenolics. Ammonia represents the most severe potential environmental hazard because of the toxicity of undissociated ammonia to aquatic organisms. This toxicity is pH dependent and is directly related to the concentration of undissociated ammonia (22). Since most coal gasification processes have the potential to discharge large volumes of ammonia contaminated alkaline wastewaters, the undissociated ammonia fraction could reach toxic levels in the receiving water. Treatment for ammonia removal is, therefore, a primary concern before aqueous wastes from coal conversion processes are discharged.

The quantity of ammonia in a gas liquor depends upon factors such as the original nitrogen content of the coal, the duration of carbonization, the amount of steam used, and the length of time the gases are exposed to radiant heat. The ammonia is present as both "free" and "fixed" ammonia. (So-called free ammonia is the ammonium ion that is largely chemically compensated by an equivalent amount of bicarbonate and carbonate alkalinity, and this ammonia can be stripped from solution without pH adjustment. The remaining fraction is called "fixed ammonia" for which pH adjustment is required during

stripping.) The residual ammonia after free leg stripping is usually difficult to strip because a given coal gasification wastewater may not have sufficient alkalinity to consume acid liberated from the ammonium ion which brings the pH down during the stripping operation. The difficulties reported with the stripping of ammonia from Lurgi wastewaters is due to the presence of high molecular weight, heterocyclic compounds which contain nitrogen (7). This nitrogen is reported as ammonia-nitrogen in the analytical results. These heterocyclic compounds are relatively nonvolatile and, therefore, difficult to strip from the gas liquor.

In the case of cyanide, available data on the acute toxicity of simple cyanides to fish reveals that the minimum lethal (threshold) concentrations of free cyanide are usually less than 250 ppb (22). It is generally acknowledged that free cyanide concentrations in the range from 50 to 100 ppb as cyanide have proven eventually fatal to many sensitive fishes and levels much above 200 ppb probably are rapidly fatal to most fish species. Cyanide, a monodentate ligand, will complex with many metals and as such, has the potential of bioaccumulating in aquatic plants and animals. The long-term effects of complexed cyanide in the aquatic environment have not been investigated adequately to determine separate water quality criteria regarding chronic toxicity impacts.

Phenolics represent an environmental hazard that is somewhat lower in magnitude than that of cyanide. Phenolic compounds can affect freshwater fishes adversely by direct toxicity to fish and fish-food organisms; by lowering the amount of available oxygen because of the high oxygen demand of the compounds and by tainting of fish flesh. Phenolic toxicity in the aquatic environment is enhanced by lower dissolved oxygen concentrations, increased salinity, and increased temperature (22). A major aesthetic problem associated with phenolic compounds is their organoleptic properties (i.e., ability to affect one or more organs of the body) in water and fish flesh.

The degree of hazard exhibited by sulfide to aquatic animal life is dependent on the temperature, pH, and dissolved oxygen level of the receiving water. At lower pH values a greater proportion of the sulfide is in the form of toxic undissociated H_2S . In winter when the pH is neutral or mildly acidic, the hazard from sulfides is increased (22). This hazard is exacerbated when dissolved oxygen levels are low (but not lethal to fish).

The major metals in coal gasification wastewaters are boron, cadmium, copper, lead, selenium, and zinc. These metals were found in each of the different coal gasification wastewaters at varying concentration levels. All are toxic to animals and man, except boron which like cadmium has phytotoxic properties. Some of these metals present a particular environmental concern because they have the potential to bioaccumulate, thereby producing a chronic poisoning effect. Boron is a pollutant that represents environmental hazard only with regard to agricultural water use. Boron is toxic to a number of sensitive plants. From the extensive work on citrus, one of the most sensitive crops, a maximum concentration of boron of 0.75 mg/L in water for long term irrigation on sensitive crops has been established by the U. S. Environmental Protection Agency (22).

Metals which have a measurable environmental impact and are also acutely toxic to man are cadmium, selenium, and lead. Allowable levels in domestic water supplies are 10 ug/L for cadmium and selenium and 50 ug/L for lead. However, the allowable concentrations in the aquatic environment for protection of certain fresh water animals are considerably lower. Although these metals are present in coal gasification wastewaters at relatively low concentrations, they still present the potential for severe environmental hazard due to progressive, chronic poisoning.

Two additional metals that are also found in coal gasification wastewaters, copper and zinc, are at a much lower environmental hazard. The toxicity of copper to aquatic life is dependent on the alkalinity of the receiving water as the copper ion is complexed by anions, which affect

toxicity. At lower alkalinity copper is generally more toxic to aquatic life. Other factors affecting copper toxicity include pH and organic compounds. The toxicity of zinc to aquatic life is impacted by the hardness, dissolved oxygen, and temperature of the receiving water. Allowable concentrations for copper and zinc in domestic water supplies are 1000 ug/L and 5000 ug/L, respectively (22). For the protection of freshwater and marine aquatic life, allowable concentrations are based on bioassay results using sensitive aquatic resident species.

ENVIRONMENTAL MONITORING REQUIREMENTS

The preceding sections presented screening test results for potential pollutants in aqueous wastes generated from the gasification of alternative coal types in both fixed-bed and entrained-bed gasifiers. These wastewater data are characteristic of large scale gasifier operations for the production of low heating value fuel gas or synthesis gas. Although the nature of the wastewaters and their respective chemistries varied greatly between gasification processes, it was possible to establish a general listing of pollutant parameters that should be monitored in the aqueous discharges from a given coal conversion facility. Given the similarities between gasifiers in the tar producing and non-tar producing categories, two aqueous waste environmental monitoring matrices can be established for gasification processes that produce quench condensates. These monitoring matrices include both conventional and nonconventional pollutants.

Tar Producing Gasifiers with Quench/Scrubbing

Candidate wastewater conventional pollutants in this gasification category are biochemical oxygen demand, chemical oxygen demand, suspended solids, dissolved solids, oil and grease, and pH. Candidate wastewater nonconventional pollutants are phenol, cresols, aromatic hydrocarbons, ammonia, sulfide, sulfite, thiosulfate, thiocyanate, cyanide (free and total), phosphorus, copper, cadmium, selenium, lead, and zinc.

Non-tar Producing Gasifiers with Quench/Scrubbing

Candidate wastewater conventional pollutants in this gasification category are biochemical oxygen demand, chemical oxygen demand, suspended solids, dissolved solids, oil and grease, and pH. Candidate nonconventional pollutants are ammonia, sulfide, sulfite, thiosulfate, thiocyanate, cyanide (free and total), boron, cadmium, and zinc.

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APPENDIX A
GASIFIER OPERATING CONDITIONS

TABLE A-1. CHAPMAN GASIFIER STREAM FLOW RATE DATA

Stream	Flow rate, g/s-gasifier ^a
Inputs:	
Coal	152
Air	385
Steam (water vapor)	80
Outputs:	
Cooled product gas	495
Gasifier ash (dry basis)	9.3
Cyclone dust	0.8
By-product tar	15

^aAverage for the two operating gasifiers.

Reference: (3).

TABLE A-2. WELLMAN-GALUSHA (FORT SNELLING) GASIFIER STREAM FLOW RATE DATA

Stream	Flow rate, g/s-gasifier	
	Sampling Period One	Sampling Period Two
Inputs:		
Coal	320 $\pm$ 28	250 $\pm$ 21
Air	500 $\pm$ 55	444 $\pm$ 49
Steam (water vapor)	67 $\pm$ 8.4	66 $\pm$ 8.3
Outputs:		
Dry product gas	720 $\pm$ 63	570 $\pm$ 49
Product gas moisture	130 $\pm$ 16	120 $\pm$ 15
Tar	12 $\pm$ 1.4	9.8 $\pm$ 1.1
Gasifier ash	27 $\pm$ 2.8	21 $\pm$ 2.1
Cyclone dust	3.8 $\pm$ 1.3	-- ^a
Gasifier ash sluice water	7	7
Cyclone dust quench water	<7	--

^aDashes mean data not available.

Reference: (2).

TABLE A-3. WELLMAN-GALUSHA (GLEN-GERY) STREAM FLOW RATE DATA

Stream	Flow rate, g/s-gasifier
Inputs:	
Coal	219
Air	992
Steam (water vapor)	194
Outputs:	
Product gas	1,333
Gasifier ash	20.6
Cyclone dust	0.2
Coal hopper gas	2.2
Pokehole gas	1.7

Reference: (1).

TABLE A-4. RILEY GASIFIER STREAM FLOW RATE DATA

Stream	Flow rate, g/s-gasifier
Inputs:	
Coal (including moisture)	1,000 $\pm$ 109
Air	1,200 $\pm$ 240
Steam	350 $\pm$ 88
Service water	2,200 $\pm$ 440
Outputs:	
Product gas (dry basis)	2,300 $\pm$ 230
Moisture in gas	620 $\pm$ 61
Gasifier ash	75 $\pm$ 30
Cyclone dust	4 $\pm$ 1
Tars and oils	21 $\pm$ 4
Ash pan water	2,200 $\pm$ 440

Reference: (9).

TABLE A-5. FOSTER-WHEELER/STOIC GASIFIER STREAM FLOW RATE DATA

Stream	Flow rate, g/s-gasifier
Inputs:	
Coal (including moisture)	300 $\pm$ 30
Air	620 $\pm$ 120
Steam (water vapor)	70 $\pm$ 7
Ash pan makeup water	7 $\pm$ 4
Lock hopper purge steam	16 $\pm$ 4
Pokehole purge steam	6 $\pm$ 2
Outputs:	
Combined product gas (dry basis)	930 $\pm$ 190
Moisture in product gas	75 $\pm$ 15
Gasifier ash	35 $\pm$ 4
Moisture in gasifier ash	9 $\pm$ 0.9
Cyclone dust	0.2 $\pm$ 0.1
ESP oil	4 $\pm$ 1

Reference: (8).

TABLE A-6. LURGI-TYPE GASIFIER STREAM FLOW RATE DATA

Stream	Flow rate, g/s-gasifier
COAL PREPARATION	
Run-of-mine coal	6,667
Dryer offgas (dry basis)	22
Dryer condensate	- ^a
Dried coal	4,444
GASIFICATION/GAS QUENCH	
Dried coal	4,444
Oxygen	778
Steam	3,611
High pressure coal lock vent (dry basis)	65
Low pressure coal lock vent (dry basis)	5.6
Ash lock cyclone vent (dry basis)	12.4
Wet ash	750
Ash quench wastewater	720
Crude gas (dry basis)	4,675
RECTISOL AGR	
Crude gas (dry basis)	4,675
Clean product gas (dry basis)	1,275
H ₂ S-rich offgas (dry basis)	1,758
CO ₂ -rich offgas (dry basis)	1,725
Cyanic water	172
Naphtha	36
GAS LIQUOR SEPARATION	
Cyanic water	172
Heavy tar	28
Waste gas (dry basis)	12.4
Medium oil	69
Light tar	111
Phenolic water	3,611
PHENOSOLVAN/STRIPPING	
Phenolic water	3,611
Crude phenol	25
NH ₃ stripper vent gas	96.5

^aDashes mean data not available.

Reference: (6)

TABLE A-7. TEXACO GASIFIER STREAM FLOW RATE DATA

Stream	Flow rate, g/s-gasifier	
	Period One ^a	Period Two ^b
Inputs:		
Coal (dry basis)	1,690	1,634
Oxygen	1,564	1,561
Fresh water ^c	1,319	347
Demineralized water	1,424	1,278
Outputs:		
Scrubbed synthesis gas	3,221	3,206
Slag	570	501
Flash gas	7.5	8.3
Settler underflow-blowdown	2,141	1,029

^aNo recycle of clarifier underflow.

^bMinimization of fresh water makeup by recycle of clarifier underflow.

^cIncludes water in coal feed, additive mixture, and flocculant mixture.

Reference: (11).

TABLE A-8. KRW PDU GASIFIER STREAM FLOW DATA

Stream	Flow Rate, g/s-gasifier		
	Test 1 Wyoming Subbituminous	Test 2 Pittsburgh No. 8	Test 3 North Dakota Lignite
<u>Inputs</u>			
Coal	219.2	141.0	271.6
Steam	56.8	73.4	67.2
Oxygen	112.8	145.3	135.6
CO ₂ to gasifier	50.8	65.7	49.2
H ₂ O injection	0.0	150.3	0.0
Coal lockhopper gas (CO ₂)	4.0	2.6	5.0
Ash lockhopper gas (CO ₂)	1.7	1.7	1.7
Makeup water	479.4	207.9	161.3
<u>Outputs</u>			
Scrubbed and cooled product gas	364.0	321.9	453.8
Gasifier ash	11.6	16.0	15.6
Wastewater	506.1	408.1	202.4
Sludge	51.8	13.8	37.7
Coal lockhopper vent	3.5	2.3	4.2
Ash lockhopper vent	1.7	1.7	1.7

Reference: (12).

TABLE A-9. KOPPERS-TOTZEK GASIFIER STREAM FLOW RATE DATA

Stream	Flow Rate, g/s-gasifier
Inputs:	
Pulverized coal	1,750
Oxygen	1,640
Steam	175
Outputs:	
Raw gas (dry)	3,110
Slag	80
Discharge water	2,275
Fly ash (dry)	210

Reference: (10).

APPENDIX B

SYNTHANE PILOT-PLANT DATA

TABLE B-1. INFLUENCE OF COAL INJECTION ON PROCESS CONDENSATE POLLUTANT PRODUCTION^a

Pollutant	By-Product Coke	Synthane PDU ^b		
		Free Fall Injection	Shallow Bed-Injection	Deep Bed-Injection
Tar	46.5	37.1 ± 13.5	5.1 ± 2.5	3.2 ± 1.1
Phenol	0.43-0.49	6.0 ± 0.7	1.8 ± 0.9	0.3 ± 0.3
Chemical Oxygen Demand	2.0-2.8	38.9 ± 7.2	5.9 ± 2.7	1.8 ± 1.2
Total Oxygen Demand	0.8-0.98	11.0 ± 1.7	2.4 ± 0.6	1.4 ± 0.4
Cyanide	0.009-0.027	-- ^c	-- ^c	-- ^c
Thiocyanate	0.16-0.18	0.02 ± 0.04	0.008 ± 0.001 ^d	0.008 ± 0.002 ^d

^aAll units as kilogram per metric ton of coal, MAF.

^bGasification of North Dakota Lignite.

^cDashes mean negligible.

^dMeasurements at or below the limiting sensitivity of the analytical method employed.

Reference: (26).

TABLE B-2. INFLUENCE OF OXYGEN SOURCE ON PROCESS CONDENSATE POLLUTANT PRODUCTION^a

Effluent Parameter	Effluent Production Levels (kg/metric ton coal, MAF)			
	North Dakota Lignite		Illinois No. 6	
	Steam-Oxygen	Steam-Air	Steam-Oxygen	Steam-Air
Tar	19.5 ± 9 ^b	29.5 ± 23	62 ± 5	103 ± 27
Phenol	4.2 ± 1.2	2.6 ± 1.1	4.9 ± 0.7	2.2 ± 0.4
Chemical oxygen demand	21 ± 5.5	13 ± 5	23 ± 2.5	21 ± 6.5 ^c
Ammonia	7.4 ± 0.9	5.5 ± 2.2 ^c	13.2 ± 4	6.2 ± 0.8
Cyanide (x10 ⁻³)	0.1 ± 0.2	0.5 ± 0.4	0.7 ± 0.2	1.8 ± 0.5
Thiocyanate (x10 ⁻²)	1.1 ± 0.9	1.3 ± 0.5 ^c	17 ± 8.9	21.5 ± 2.3

^aFree fall gasification trials with Synthane PDU.^bAverage ± one standard deviation from the mean.^cSignificant statistical difference from steam-oxygen production at 95% confidence level.

Reference: (26).